



Power Goals for Human Space Exploration



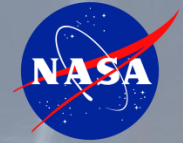
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National Aeronautics and
Space Administration



Outline



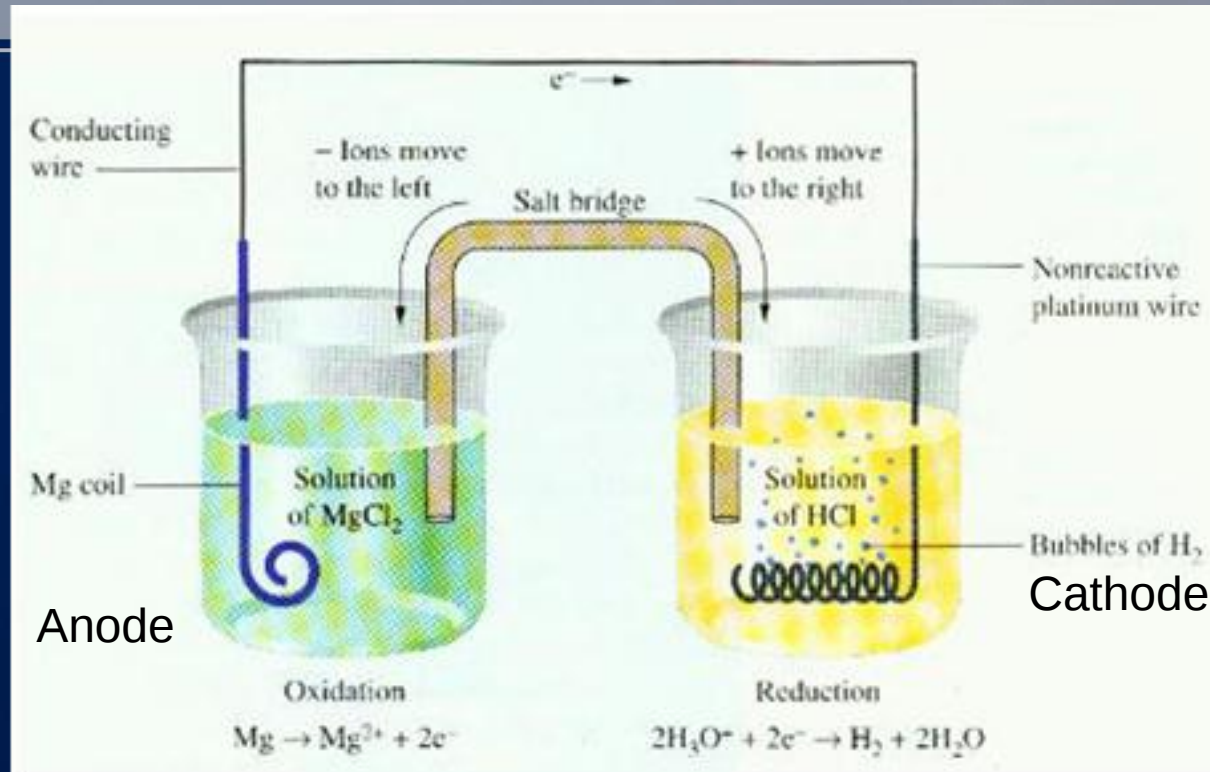
- Battery Basics
- Battery Chemistries commonly used for Human Space Exploration
- Current and Future Missions
- Technology Programs to Achieve Power Goals
- Challenges
- Summary



Basic Battery Equations

- $E \text{ (Volts)} = I \text{ (Amperes)} * R \text{ (Ohms)}$
- E : Voltage; I : Current; R : Resistance
- $P \text{ (Watt)} = I \text{ (Amperes)} * E \text{ (Volt)}$
- P : Power

Simple Galvanic Cell

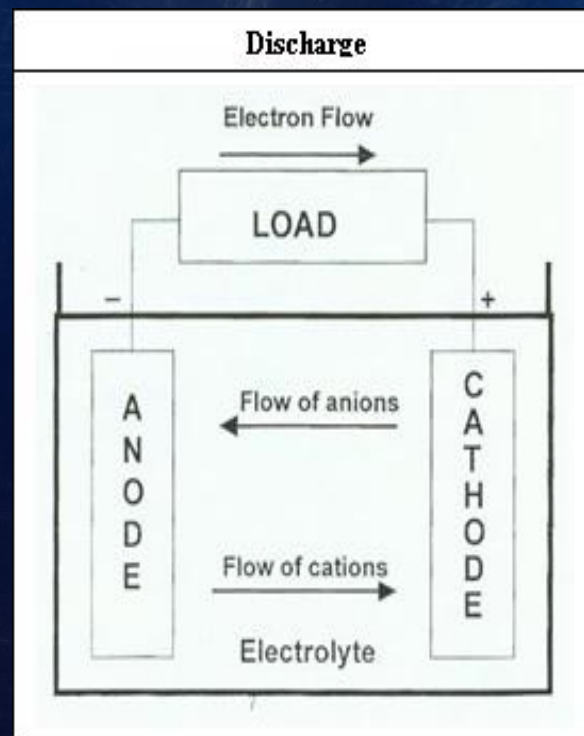
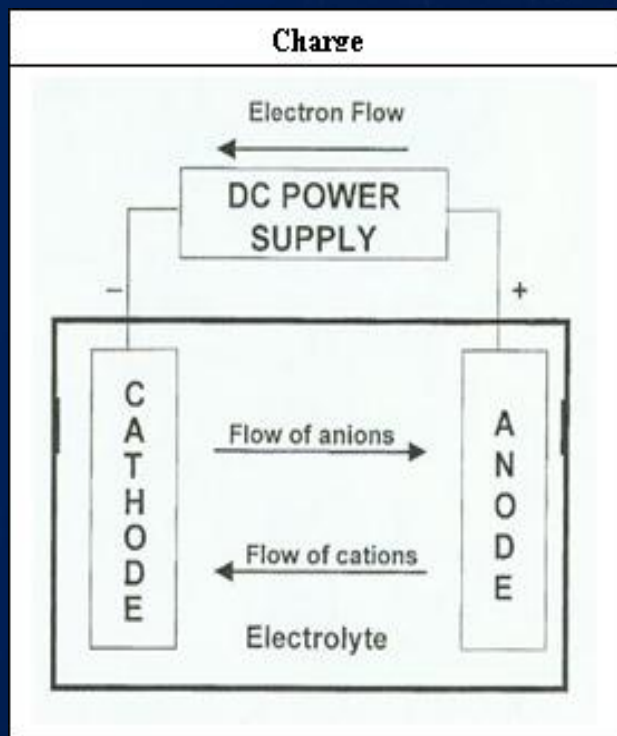


Oxidation half reaction (Anode): $\text{Mg}_{(\text{s})} \rightarrow \text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^-$

Reduction half-reaction (Cathode): $2\text{H}_3\text{O}^+_{(\text{aq})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$

Sum: $\text{Mg}_{(\text{s})} + 2\text{H}_3\text{O}^+_{(\text{aq})} \rightleftharpoons \text{H}_{2(\text{g})} + \text{Mg}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$

Charge and Discharge Electrochemistry



Battery Terminology:
Cathode is always the positive electrode
Anode is always the negative electrode

Electrochemical Equations

- $E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}}$
- $W_{\text{max}} = -n \cdot F \cdot E_{\text{cell}} = \Delta G$
- $-n \cdot F \cdot E_{\text{cell}}^0 = \Delta G_{298}^0$
- For a reaction to occur spontaneously, ΔG should be negative (implies that E should be always positive).
- Nernst Equation:
 - $E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF) \cdot \ln(Q)$
 - For the following reaction,
 - $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$
 - $Q = \text{reaction quotient} = [P_C]^x [P_D]^y / [P_A]^m [P_B]^n$

Major Classification of Batteries

Primary Cells or Batteries:

- These cells or batteries are discharged once and discarded.

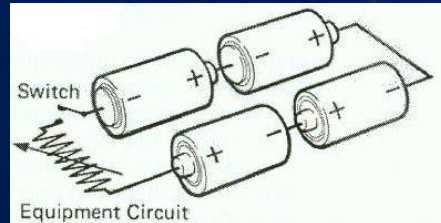
Secondary or Rechargeable Cells or Batteries:

- These batteries can be recharged after discharge. They are also called storage batteries or accumulators.

Reserve Batteries:

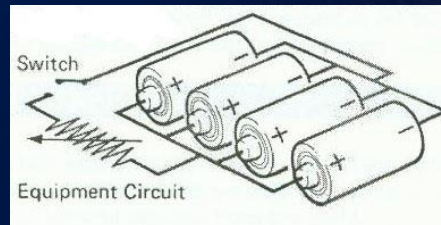
- In this type of primary battery, a key component is kept separate from the rest of the battery until activation. By doing this, chemical deterioration and self-discharge are essentially eliminated. Usually the electrolyte is the component separated. However, in thermal batteries, the electrolyte is solidified until heated and melted to activate the battery, eg. Na/S.

Battery Configuration



Voltage is additive, capacity is not and remains the same as for a single cell.

Series Configuration (string)



Capacity is additive, voltage is not and remains the same as for a single cell.

Parallel Configuration (bank)

Factors to Consider in Choosing a Battery

- Performance (voltage and capacity) including any pulse requirements
- Volumetric and Gravimetric Energy Density
- Safety
- Toxicity
- Thermal capability
- Cycle / service life
- Calendar life
- Unique environments
- Cost

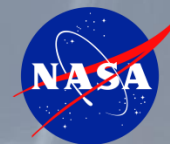
Energy and Toxicity

- Two main factors that categorize safety
- Energy provided in Wh/kg or Wh/L – categorization and waivers provided under each chemistry
- Toxicity – based on electrolyte (vapors, decomposition products, etc.)

General Tox information based on NASA ratings:

- KOH: alkaline, NiCd, NiMH, AgZn – caustic and corrosive- will burn skin and eyes. Typically Tox 2.
- H₂SO₄: Lead acid- acidic and corrosive, will create acid fumes that can damage throat and lungs. Typically Tox 2 unless the amount is significantly large.
- SOCl₂: LiSOCl₂, LiSO₂Cl₂, LiSO₂ and LiBCX- burn skin, eyes, damage throat and lungs to a higher degree than above and can be lethal. Tox 4; could be lower if electrolyte quantity is negligible.
- Li-ion, Li(CF)_x and LiMnO₂: Corrosive electrolyte that affects skin and eyes on contact (permanent eye injury to crew); electrolyte is flammable and can cause fire in the presence of an ignition source. Tox 2 based on nature of salt in electrolyte.

NASA Human-Rated Li-ion Battery Applications



Current: Flying Li-ion since 1999

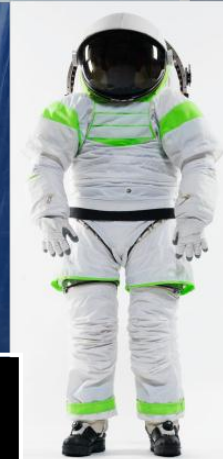
- Government furnished equipment ~ 20 types (< 20V/ 10 Ah)
- Experiments/Payloads (55 to 60 types) up to 270 V (high energy, high power, capacity 2 to 20 Ah)
- Crew suit (main power) 20 V/ 40 Ah
- Space vehicles and Space Launch Systems
 - HTV (32 V / 174 and 100 Ah), SpaceX (28 V/ 200 Ah and 28 V/16.5 Ah)

Future (and in work):

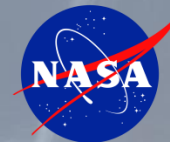
- ISS Main Power (120 V / 134 Ah)
- Robonaut (106 V / 60 Ah)
- New Tools (18 V to 28 V / 8Ah)
- New Vehicles (Orion 120V/ 30Ah; Orion LAS 140V 10Ah, 28V 1Ah; Orbital, 28 V/190 Ah; Boeing, SNC, Blue Origin)
- Surface mobility systems (270 V / 60 Ah high power)
- Lunar Lander Platforms (varying); Habitats (≥ 28 V)

Uniqueness:

- Space, confined volume and human-rated with zero tolerance to fire
- pressurized and unpressurized environments



NASA Non-Human-Rated Li-ion Battery Applications



Deep Space Missions:

First Mission in 2002 (Maj. 20-70 Ah;
One at 120 Ah)

Current:

- Mars Exploration Rover (Spirit and Opportunity)
- Mars Phoenix Lander
- Juno (Jupiter Orbiter)
- Kepler
- NuStar
- GRAIL
- Aquarius
- Mars Science Laboratory
- SMAP (On-going) and

Future:

- Europa Orbiter
- Mars 2020 Rover
- Mars Insight (Lander)

Satellite Applications:

First Mission in 2006 (6 Ah to 134 Ah)

Current:

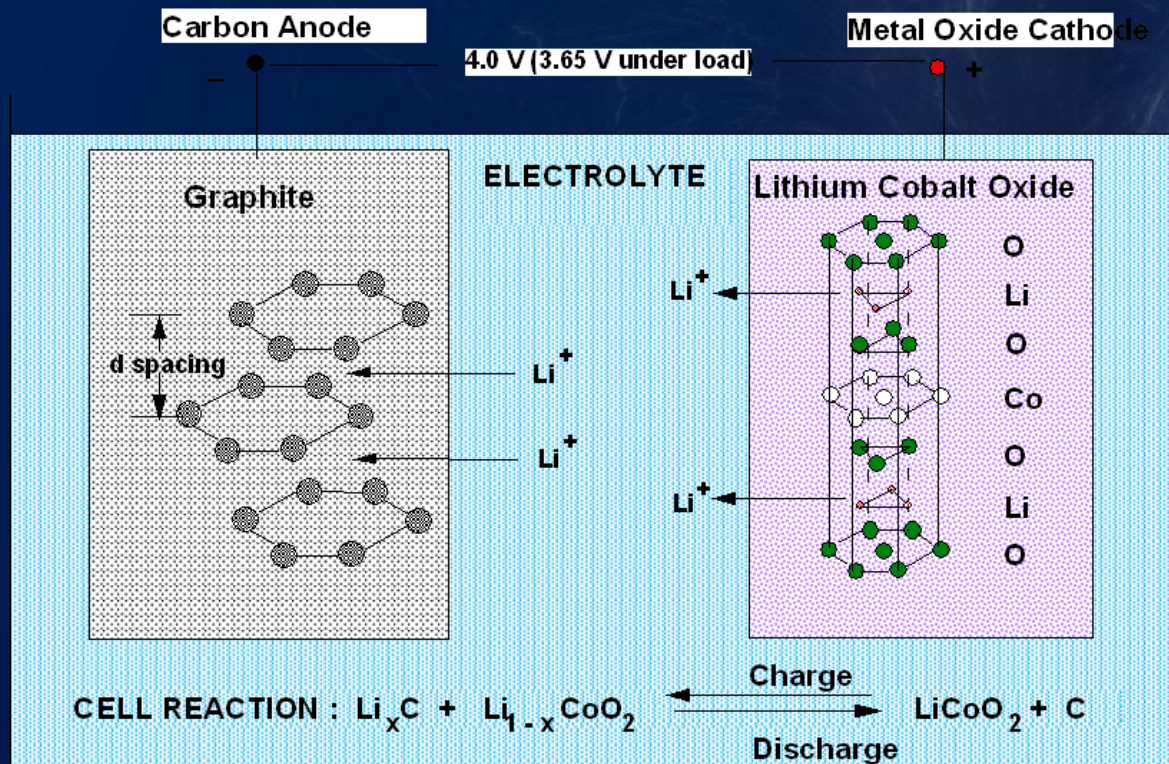
- Lunar Reconnaissance Orbiter (LRO)
- Solar Dynamics Observatory (SDO)
- Van Allen Probes (formerly RBSP Radiation Belt Storm Probes)
- Interstellar Boundary Explorer (IBEX)
- ST-5 (mission completed)

Future:

- Global Precipitation Measurement (GPM) spacecraft
- Magnetospheric Multiscale (MMS) spacecrafts
- Mars Atmosphere and Volatile Evolution (MAVEN)
- DSCOVR (Triana) spacecraft
- James Webb Space Telescope (JWST)
- Joint Polar Satellite System-1 (JPSS-1)
- Solar Probe Plus
- Ice, Cloud and Land Elevation Satellite -2 (ICESAT-2)
- GeoStationary Operational Environmental Satellite (GOES-R)



Li-ion Cell Schematic



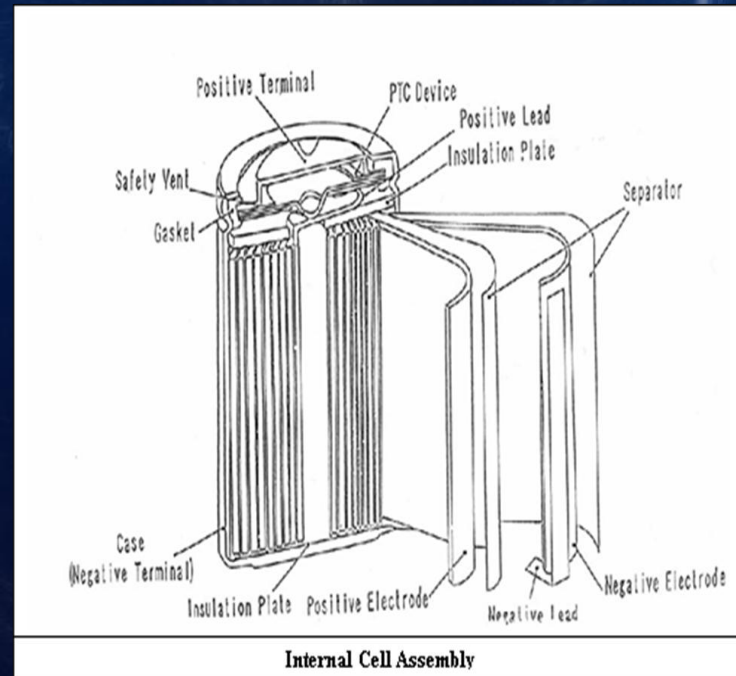
Battery Terminology:

Cathode is always the positive electrode

Anode is always the negative electrode

Components of a Cell

1. Cathode: **The positive electrode of the cell (for discharge).**
2. Anode: **The negative electrode of the cell (for discharge).**
3. Electrolyte: **The medium that provides the ion transport mechanism between the positive and negative electrodes in a cell. (This can be aqueous or non-aqueous)**
4. Separator: **A microporous material that keeps the cathode and anode from touching each other.**



Li-ion Cell Reactions

- Anode: Carbon compound (graphite); copper current collector (titanate in some cases)
- Cathode: Lithium metal oxide such as LiCoO_2 , $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, LiNiO_2 , LiV_2O_5 , LiMn_2O_4 , $\text{LiNiO}_{0.2}\text{Co}_{0.8}\text{O}_2$, and several other combinations of mixed oxides as well as mixtures of metal oxides; Al current collector
- Electrolyte: Mixture of organic carbonate solvents with LiPF_6 salt
- The half reactions are:
Cathode: $\text{LiMO}_2 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^-$
Anode: $\text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}$
- The overall reaction is: $\text{LiMO}_2 + \text{C} \rightleftharpoons \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2$
- Where LiMO_2 represents the lithiated metal oxide intercalation compound.

Key Performance Parameters for Battery Technology Development

Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/controllers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a moderate reduction in the performance with flame retardants and non-flammable electrolytes	Benign cell venting without fire or flame and reduce the likelihood and severity of a fire in the event of a thermal runaway	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and external short circuit with no fire or flame
Specific energy <u>Lander:</u> 150 – 210 Wh/kg 10 cycles <u>Rover:</u> 150 – 200 Wh/kg <u>EVA:</u> 200 – 300 Wh/kg 100 cycles	Battery-level specific energy*	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	130 Wh/kg at C/10 & 30°C 120 Wh/kg at C/10 & 0°C	135 Wh/kg at C/10 & 0°C “High-Energy”** 150 Wh/kg at C/10 & 0°C “Ultra-High Energy”**	150 Wh/kg at C/10 & 0°C “High-Energy” 220 Wh/kg at C/10 & 0°C “Ultra-High Energy”
	Cell-level specific energy	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	150 Wh/kg at C/10 & 0°C	165 Wh/kg at C/10 & 0°C “High-Energy” 180 Wh/kg at C/10 & 0°C “Ultra-High Energy”	180 Wh/kg at C/10 & 0°C “High-Energy” 260 Wh/kg at C/10 & 0°C “Ultra-High Energy”
	Cathode-level specific capacity Li(Li,NiMn)O ₂	140 – 150 mAh/g typical	Li(Li _{0.17} Ni _{0.25} Mn _{0.58})O ₂ : 240 mAh/g at C/10 & 25°C Li(Li _{0.2} Ni _{0.13} Mn _{0.54} Co _{0.13})O ₂ : 250 mAh/g at C/10 & 25°C 200 mAh/g at C/10 & 0°C	260 mAh/g at C/10 & 0°C	280 mAh/g at C/10 & 0°C
	Anode-level specific capacity	320 mAh/g (MCMB)	320 mAh/g MCMB 450 mAh/g Si composite	600 mAh/g at C/10 & 0°C with Si composite	1000 mAh/g at C/10 0°C with Si composite
Energy density Lander: 311 Wh/l Rover: TBD EVA: 240 – 400 Wh/l	Battery-level energy density	250 Wh/l	n/a	270 Wh/l “High-Energy” 360 Wh/l “Ultra-High”	320 Wh/l “High-Energy” 420 Wh/l “Ultra-High”
	Cell-level energy density	320 Wh/l	n/a	385 Wh/l “High-Energy” 460 Wh/l “Ultra-High”	390 Wh/l “High-Energy” 530 Wh/l “Ultra-High”
Operating environment 0°C to 30°C, Vacuum	Operating temperature	-20°C to +40°C	-50°C to +40°C	0°C to 30°C	0°C to 30°C

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

* Battery values are assumed at 100% DOD, discharged at C/10 to 3.0 volts/cell, and at 0°C operating conditions

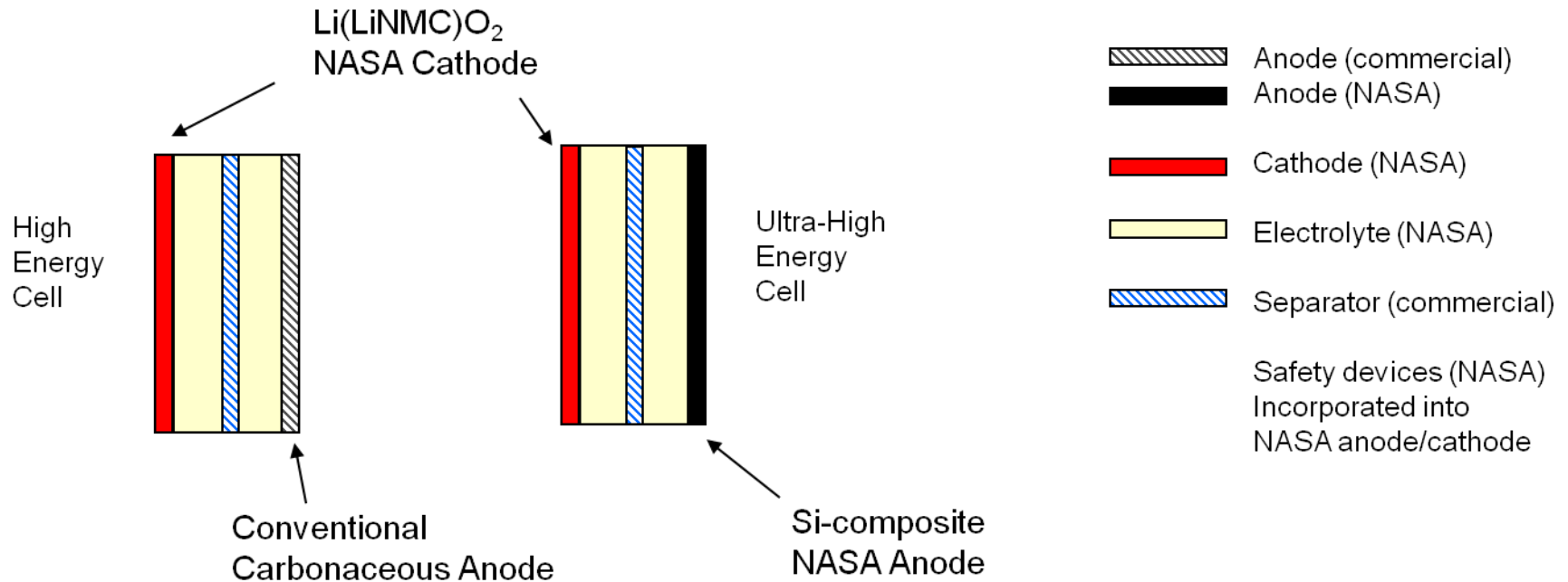
** “High-Energy” = Exploration Technology Development Program cathode with MCMB graphite anode

“Ultra-High Energy” = Exploration Technology Development Program cathode with Silicon composite anode

Space Power Systems (SPS) Li-ion Cell Development

- **Component-level goals** are being addressed through a combination of NASA in-house materials development efforts, NASA Research Announcement contracts (NRA), and grants
- Materials developed will be delivered to NASA and screened for their electrochemical and thermal performance, and compatibility with other candidate cell components
- Other activities funded through NASA can be leveraged – NASA Small Business Innovative Research (SBIR) Program and Innovative Partnership Program (IPP)
- Leveraging off other government programs (DOD, DOE) for component-level technology
- Leveraging off other venues through Space Act Agreements (SAA) that involve partnerships with industry partners such as Exxon; non-profit organizations such as Underwriters Laboratory (UL), etc.

Energy Storage Project Cell Development for Batteries



“High Energy” Cell

Baseline for EVA and Rover

Lithiated-mixed-metal-oxide cathode / Graphite anode

Li(LiNMC)O₂ / Conventional carbonaceous anode

150 Wh/kg (100% DOD) @ battery-level 0°C C/10

80% capacity retention at ~**2000** cycles

“Ultra-High Energy” Cell

Upgrade for EVA and Altair, possibly Rover

Lithiated-mixed-metal-oxide cathode / Silicon composite anode

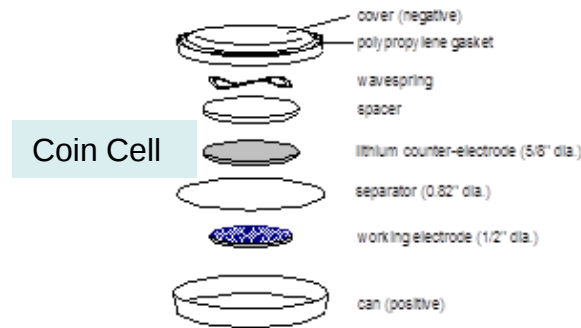
Li(LiNMC)O₂ / silicon composite

220 Wh/kg (100% DOD) @ battery-level 0°C C/10

80% capacity retention at ~**200** cycles

Cell Development

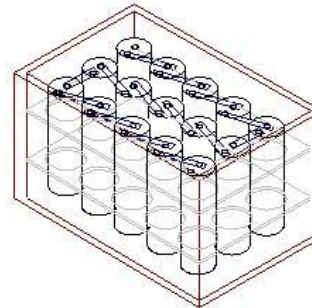
- **Assess components**
 - Build and test electrodes and screening cells (Coin and Pouch)
 - Provide manufacturing perspective from the start
- **Scale-up components**
 - Transition components from the lab to the manufacturing floor
- **Build baseline cells (10 Ah):**
 - graphite anode (MPG-111) with nickel-cobalt cathode (NCA)
 - Determine baseline performance
- **Build and test evaluation cells (10 Ah):**
 - Determine component interactions
 - Determine cell-level performance



Pouch Cell



DD Cells



Cathode Development Led by JPL

- **Goals:**
 - Specific capacity of 280 mAh/g at C/10 and 0°C to 3.0 V
 - High voltage operation to 4.8 V
 - Improved thermal stability over conventional Li-ion cathodes

Technology Challenges	Current Project Approaches to Address
High specific capacity at practical discharge rates	• Vary stoichiometry to determine optimum chemical formulation • Reduce particle size • Experiment with different synthesis methods to produce materials with physical properties such that their specific capacity is retained on production scale
Low volume per unit mass	• Vary cathode synthesis method to optimize properties that can: • Improve energy density • Improve ability to cast cathode powders • Facilitate incorporation of oxide coatings, which have the potential to increase rate capability and reduce capacity fade to extend cycle life
Minimize 1 st cycle irreversible capacity loss and irreversible oxygen loss	• Surface modification via coatings to improve cathode-electrolyte interfacial properties • Improves capacity retention • Reduces capacity fade

Cathode Materials

System	Sp. Capacity, mAh/g		Voltage vs Li	Sp. Energy, Wh/kg (Cathode Alone) vs Li	TRL	Manufacturer (and Heritage)
	Theoretical	Experimental				
LiCoO ₂ (Lithiated Cobalt Oxide)	274	137	4.15	569	7-9	ABSL (Kepler, Aquarius, SMAP, EVA)
Li(NCO) (LiNi _{0.8} Co _{0.2} O ₂)	274	165	4.05	668	7-9	Yardney (Mars Missions, MER, MSL, GRAIL, Juno)
Li(NCA) (LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂)	279	165	4.05	668	7-9	SAFT, Quallion, Yardney (Space Station, PGT)
Li (NMC) (0.33:0.33:0.33)	278	180	4.3	774	4	No
Li (Li,NMC)O ₂ Layered -layered Composites of LiMn ₂ O ₃ :LiMO ₂	330	275	4.5	1238	2-3	No
LiFePO ₄ (Olivine)	170	160	3.6	576	5	A123 (None)
LiCoPO ₄ (Olivine)	166	155	4.8	744	1-2	No
LiMnPO ₄ (Olivine)	171	160	4.3	688	1-2	No
LiMn ₂ O ₄ (Cubic Spinel)	148	120	4	480	4	No
LiMn _{1.5} Ni _{0.5} O ₄ (5 V Spinel)	148	130	4.8	624	4	No

Courtesy: Kumar
Bugga, JPL

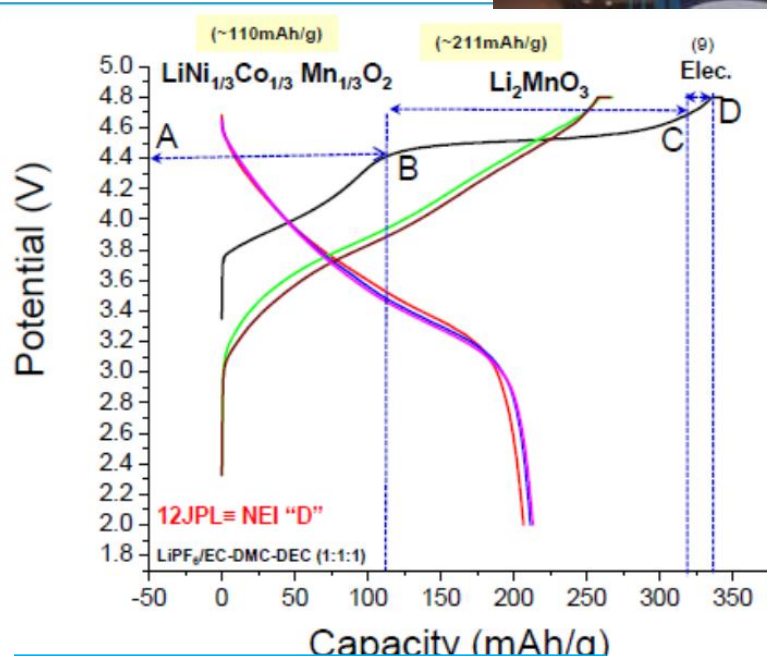
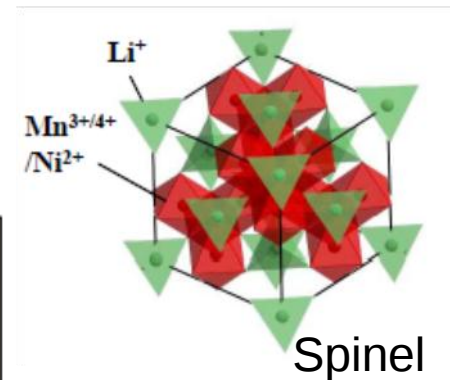
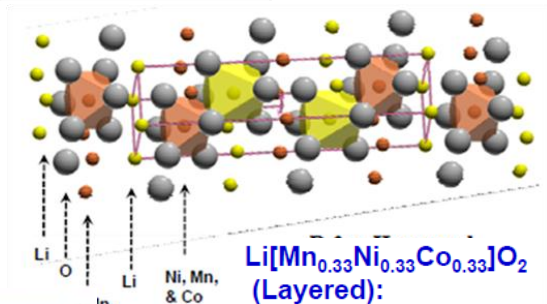
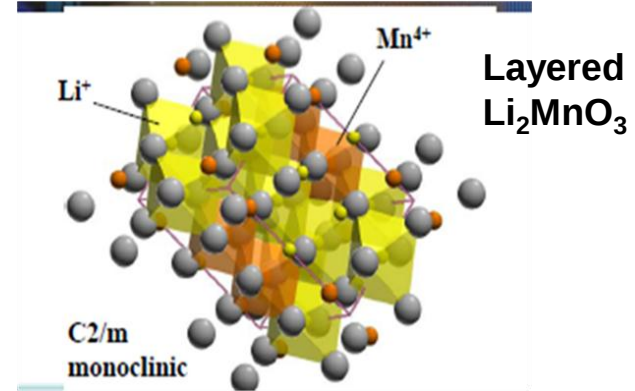
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NASA-JSC



High Specific Energy Cathodes for Li-ion cells

Why Composite Electrode?

- Bi-functional electrode: Provide high capacity through 2D layer structure and high rate capability by 3D spinel structure
- Prevent oxygen loss during charge
- Enhance cathode stability through the spinel-layered or layered-layered integrated composite structure



1st Charge Cap. Contributions:

AB:	~110 mAh/g (up to 4.4V)
BC:	~211 mAh/g (4.4 – 4.6V)
CD:	~9 mAh/g Electrolyte (> 4.6 V)

1st Discharge (calculated):

From $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$:	110
Li_2MnO_3 :	211 * 1/2: 105.5
Total:	105.5 + 110 = 215.5 mAh/g

1st cycle: $\text{Li}_2\text{Mn}^{\text{IV}}\text{O}_3 \rightarrow \text{Li}_2\text{O} + \text{MnO}_2$ (C)
 $\text{Li}^+ + \text{MnO}_2 \rightarrow \text{Li}_{1-x}\text{Mn}^{\text{III}}\text{O}_3$ (D)

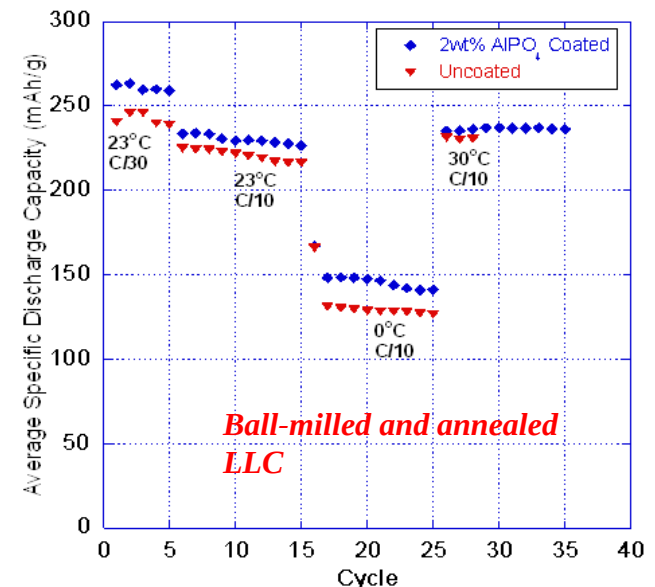
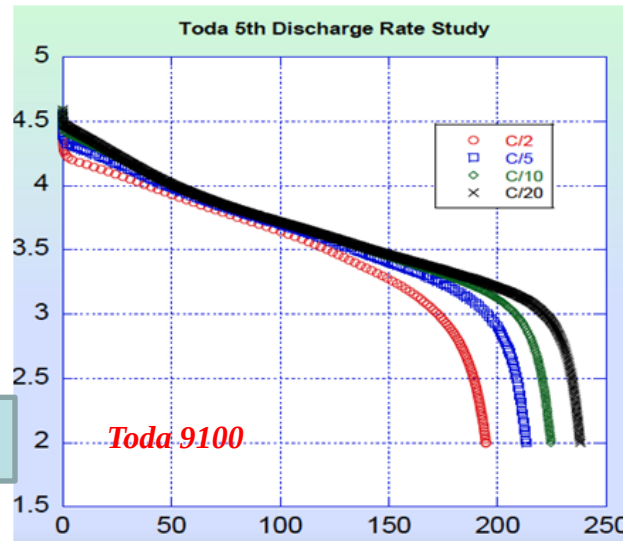
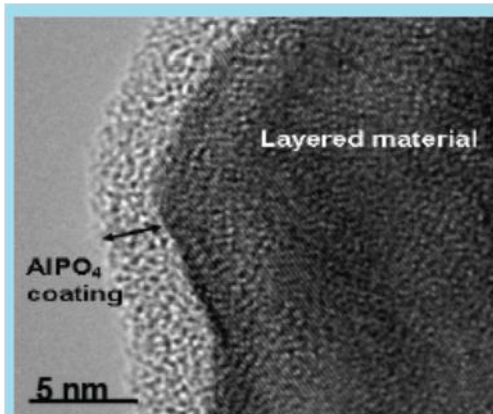
Cathode Efforts

Lithium Manganese rich Layered Layered Composites

Strategies:

- Determine best ratio of Li, Ni, Mn and Co to maximize the capacity
- Add surface coating on cathode particles to improve the interfacial properties (reduces electrolyte reactivity and facilitates charge transfer)
- Improve morphology to create ultrafine spherical particles (vary synthesis method)

- High capacity > 250 mAh/g achieved from optimized composition of transition metal ratio and Li content
- High tap densities (1.5-2.0 g/cc) and spherical morphology realized from hydroxide precursor synthesis.
- Demonstrated improved performance (high reversible and low irreversible capacity, and cyclic and thermal stability with surface coatings, (AlPO_4 & LiCoPO_4)
- Developed new efficient coatings amenable for scale-up
- Evaluated cathode material of similar composition from several commercial sources.



Courtesy: Kumar Bugga, JPL

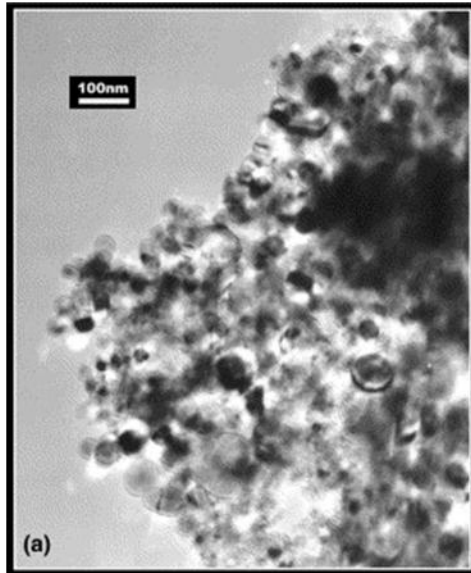
Anode Development Led by NASA GRC

- **Goal:** 1000 mAh/g at C/10 (10 hour discharge rate) and 0°C
 - Over 3 times the capacity of SOTA (State-of-the-art) Li-ion anodes
 - Threshold value = 600 mAh/g at C/10 and 0°C

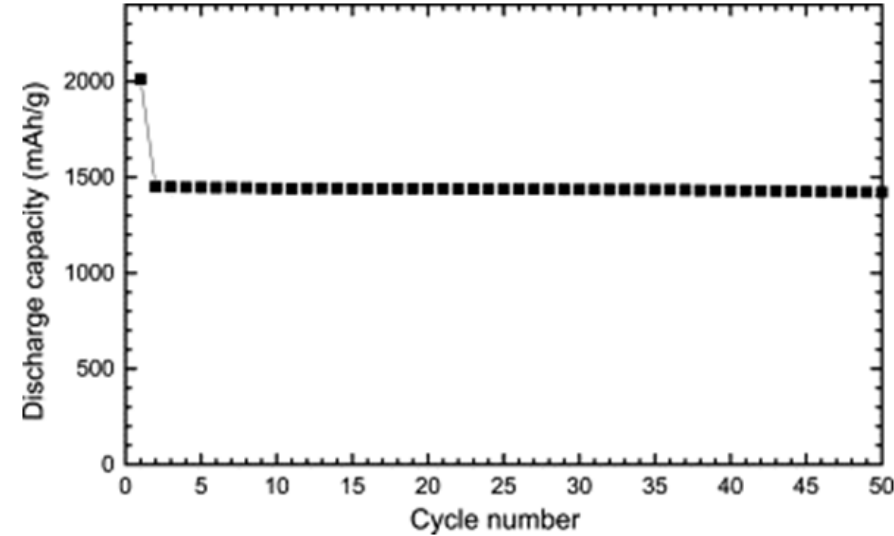
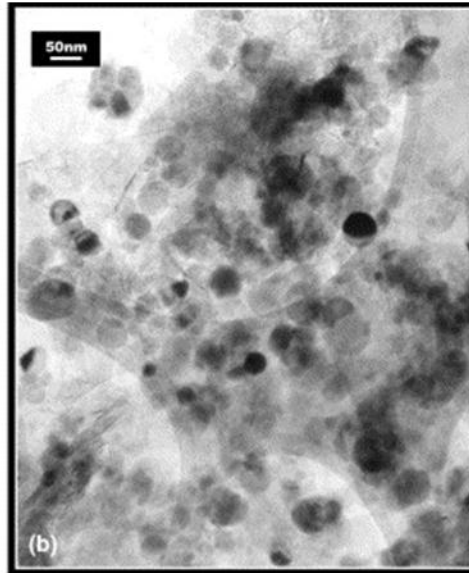
Technology Challenges	Current Approaches to Address
Minimize volume expansion during cycling	•Pursuing various approaches to optimize the anode structure to accommodate volume expansion of the silicon •Nanostructured Si composite absorbs strain, resists active particle isolation on cycling •Incorporation of elastic binders in Si –graphite and Si-C matrices •Improvement of mechanical integrity by fabricating structure to allow for elastic deformation
Minimize irreversible capacity loss	•Protection of active sites with functional binder additives •Pre-lithiation approaches are possible •Nanostructured Si resists fracture and surface renewal
250 cycles	Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life

Si-C composites

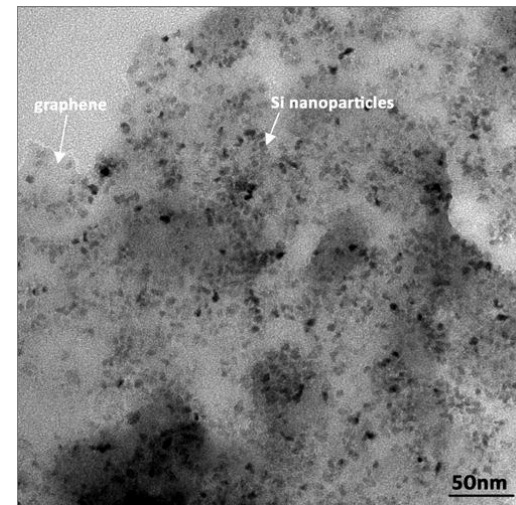
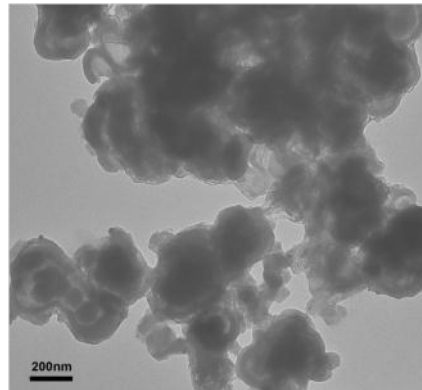
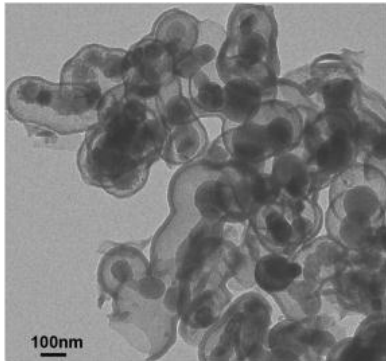
TEM of nanocrystalline Si



TEM of nanocrystalline Si-C composites

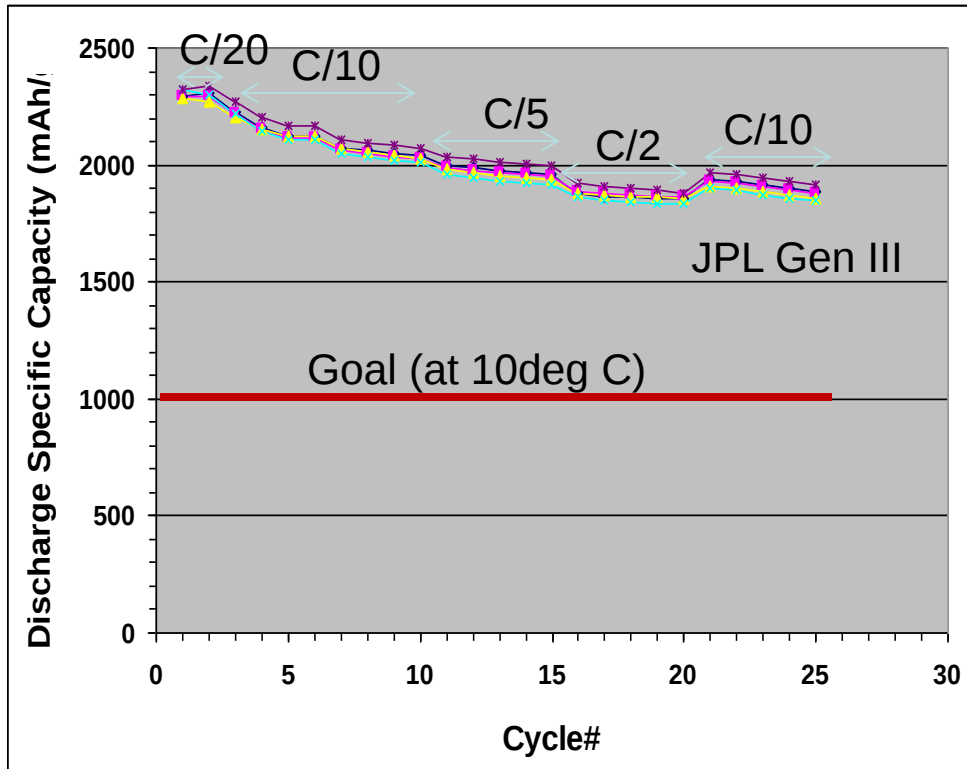


Wang, et.al Electrochem Communications, Vol 6, Issue 7, 2004,p .689

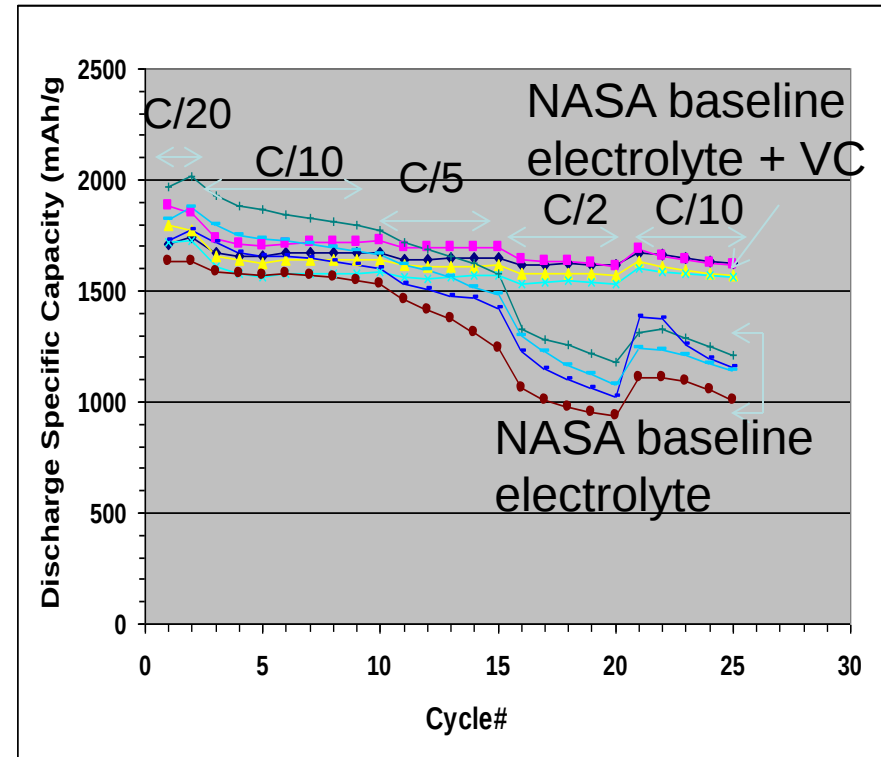


Si Anode Material Scale-up and Test

Si Anode made by Saft (2nd, calendared)



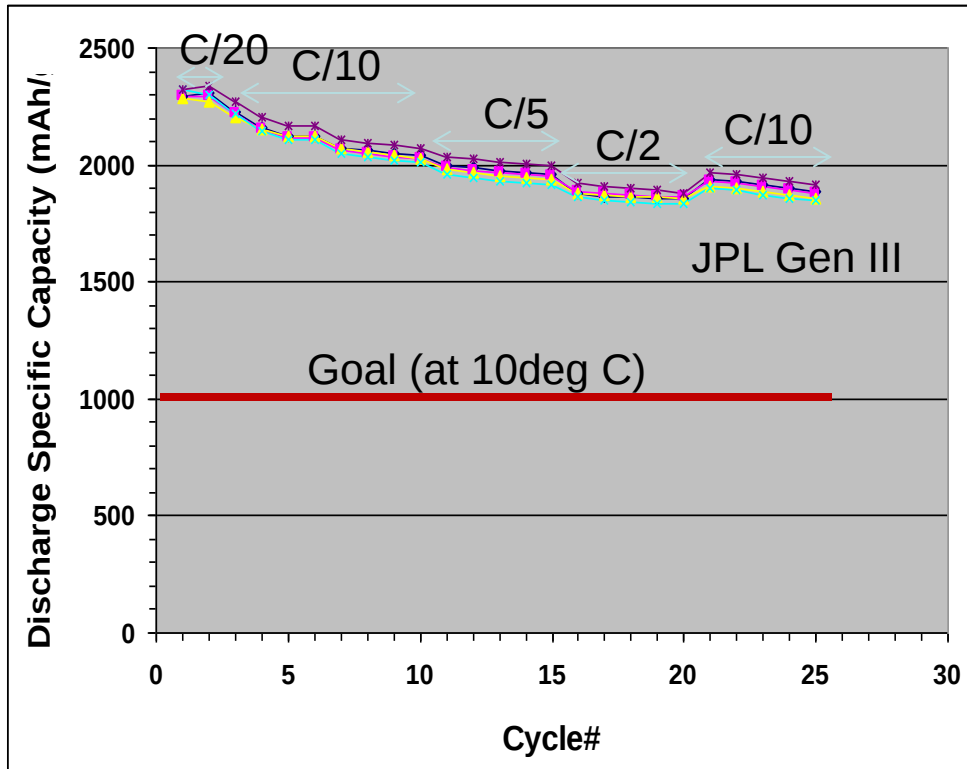
Si Anode (GT-4B)



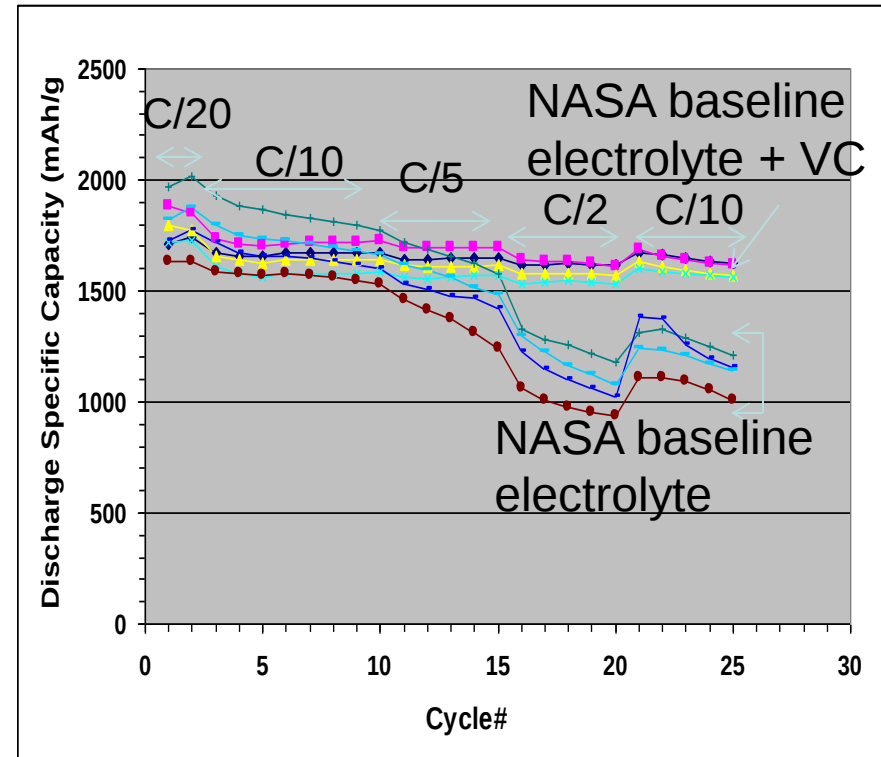
- Saft successfully scaled up Si anode:
Si anode made by Saft shows the highest capacity and excellent rate capability cycling which is much higher than 1000 mAh/g (the goal)
- VC in baseline electrolyte improves rate capability cycling

Si Anode Material Scale-up and Test

Si Anode made by Saft (2nd, calendared)



Si Anode (GT-4B)



- Saft successfully scaled up Si anode:
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- VC in baseline electrolyte improves rate capability cycling

Current State for Safety of Li-ion Batteries

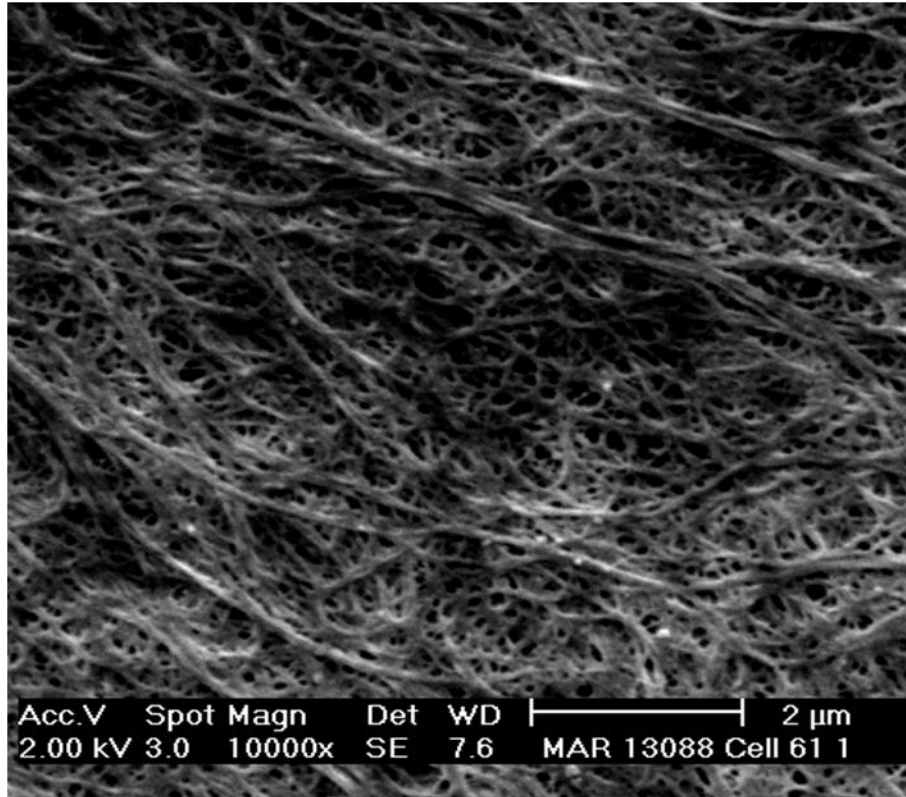
Although the chemistry is one that can provide very high energy density at this time, it is not the safest

- NASA human-rated safety requirement is **two-fault tolerance** to **catastrophic failures** – leakage of electrolyte (toxicity hazard), fire, thermal runaway

Hazards are encountered in Li-ion cells/ batteries typically during

- **Overcharge/overvoltage**
- **External shorts**
- **Repeated overdischarge with subsequent charge**
- **High thermal environments**
- **Internal Shorts**

Current Separators in Commercial-off-the-Shelf Li-ion Cells



Unactivated Separator



Activated Separator

Shut-down temperature is very close to temperature at which initiation of thermal runaway occurs.

Electrolytes

Electrolyte Selection Criteria

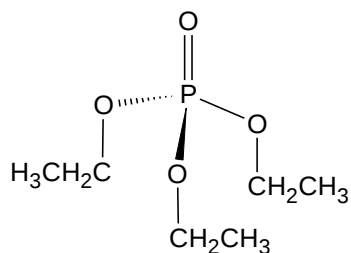
- High conductivity over a wide range of temperatures
 - 1 mS cm⁻¹ from –60 to 40°C
- Wide liquid range (low melting point)
 - -60 to 75°C
- Good electrochemical stability
 - Stability over wide voltage window (0 to 4.5V)
 - Minimal oxidative degradation of solvents/salts
- Good chemical stability
- Good compatibility with chosen electrode couple
 - Good SEI characteristics on electrode
 - Facile lithium intercalation/de-intercalation kinetics
- Good thermal stability
- Good low temperature performance throughout life of cell
 - Good resilience to high temperature exposure
 - Minimal impedance build-up with cycling and/or storage

➤ **In addition, the electrolyte solutions should ideally have low flammability and be non-toxic !!**

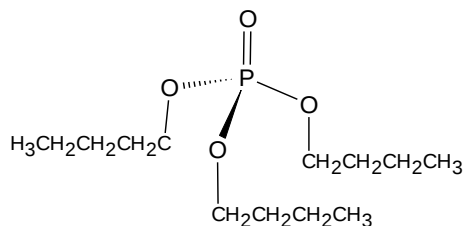
Flame Retardant Additives in Li-ion Cells for Improved Safety Characteristics

- Modification of electrolyte is one of the least invasive and cost effective ways to improve the safety characteristics of Li-ion cells. Common approaches include:
 - Use of Redox shuttles (to improve safety on overcharge)
 - Ionic liquids (have inherently low flammability, due to low vapor pressure)
 - Lithium salt modification
 - Flame retardant additives
 - Use of non-flammable solvents (i.e., halogenated solvents)
- Of these approaches, the use of flame retardant additives has been observed to possess the least impact upon cell performance.

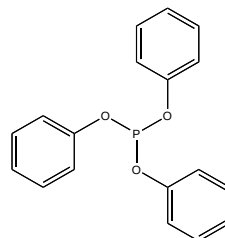
Development of Electrolytes Containing Flame Retardant Additives



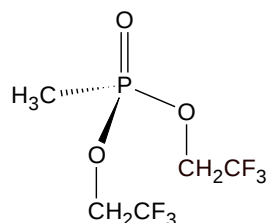
Triethyl phosphate (TEP)



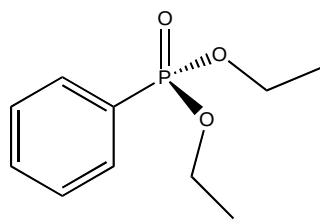
Tributyl phosphate (TBP)



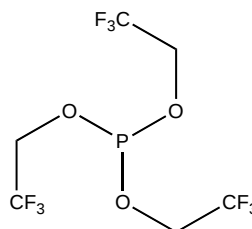
Triphenyl phosphite (TPPi)



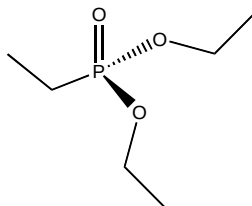
Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)



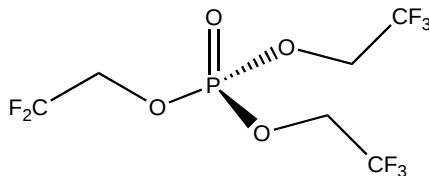
Diethyl phenylphosphonate (DPP)



Tris(2,2,2-trifluoroethyl) phosphite (TFPi)

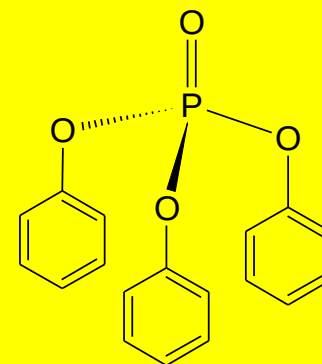


Diethyl ethylphosphonate (DEP)



Tris(2,2,2-trifluoroethyl) phosphate (TFPa)

TPP identified as being the most robust flame retardant additive

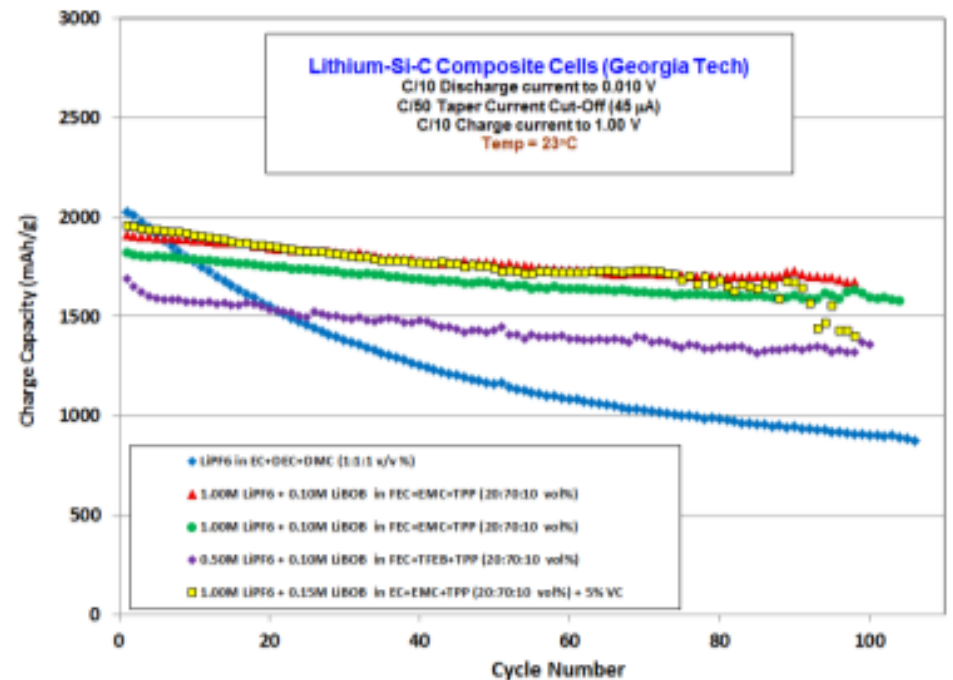
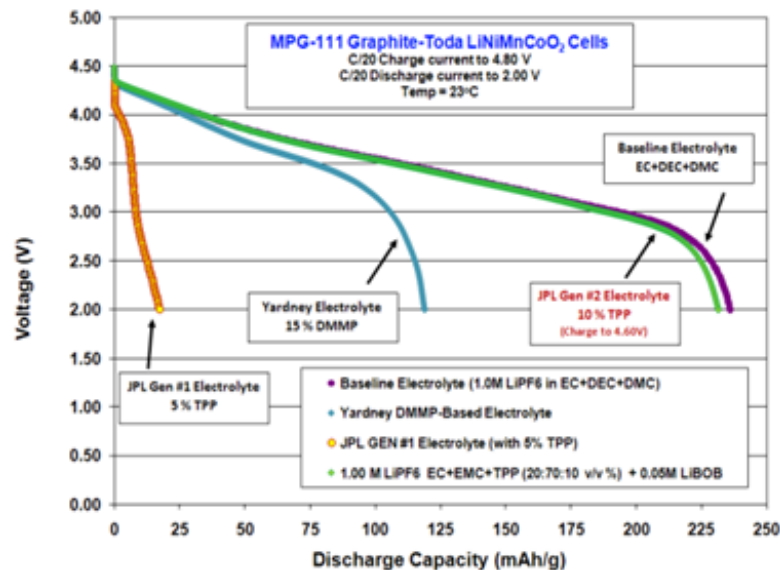


Triphenyl phosphate (TPP)

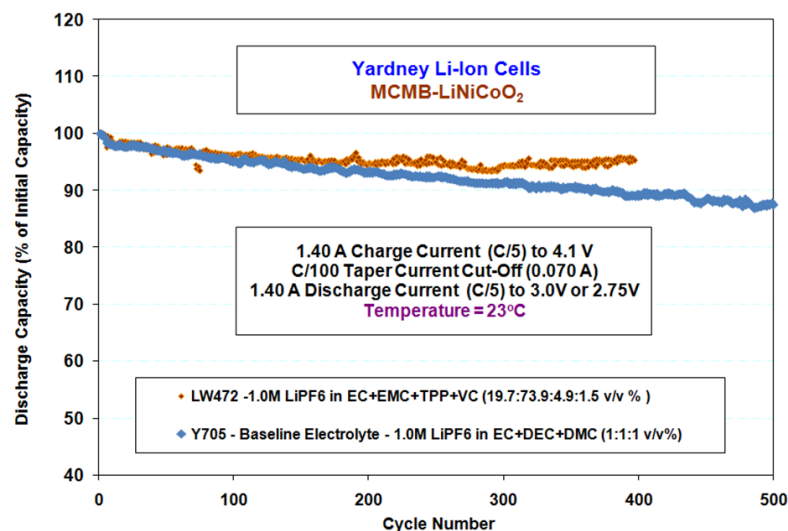
Electrolytes with the various additives were incorporated into three electrode cells with various cathodes and anodes, and Li metal reference electrodes

- 1) Y. E. Hyung, D. R. Vissers, K. Amine
J. Power Sources, **2003**, 119-121, 383
- 2) K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow
J. Electrochem. Soc. **2002**, 149, A622

Electrolytes

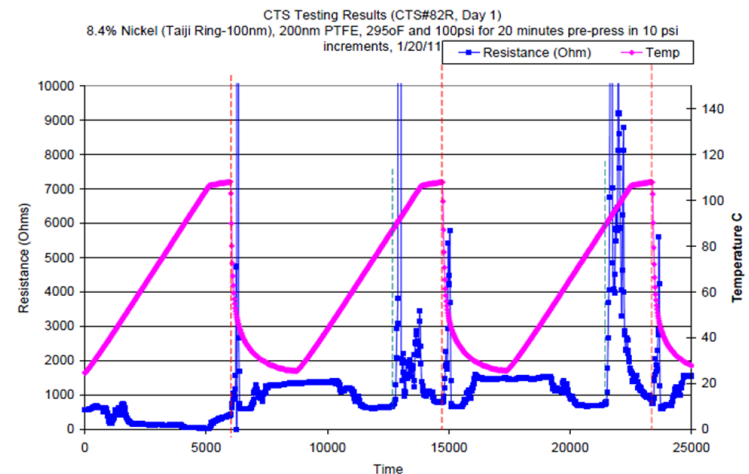
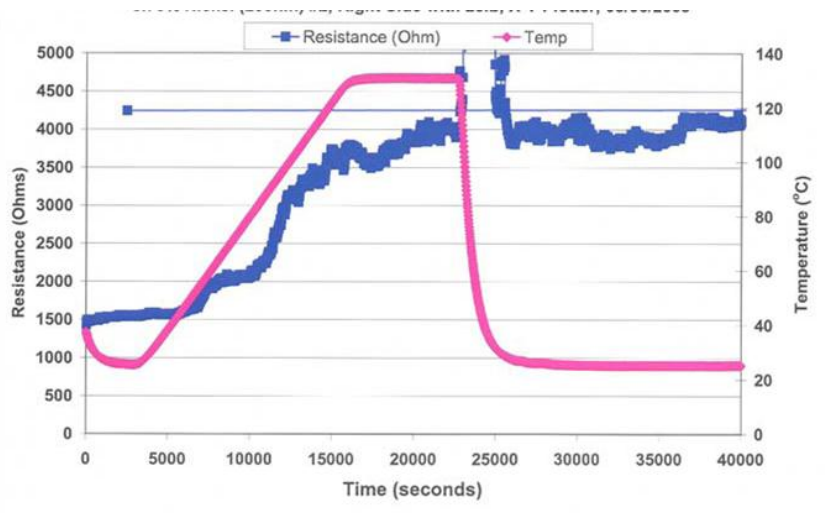


DMMP: Dimethyl
 Methyl phosphanate
 VC: Vinylene carbonate
 LiBOB: Lithium bisoxalatoborate



Safety Component Development Led by NASA JSC

- Development of internal cell materials (active or inactive) designed to improve the inherent safety of the cell
 - Approach 1: Develop a high-voltage stable (phosphate type) coating on cathode particles to increase the safe operating voltage of the cell and reduce the thermal dissipation by the use of a high-voltage stable coating material. (Nano-sized material)
 - Approach 2: Develop a composite thermal switch to shutdown cell reactions safely using coatings on the current collector substrates (nano-particle metals)



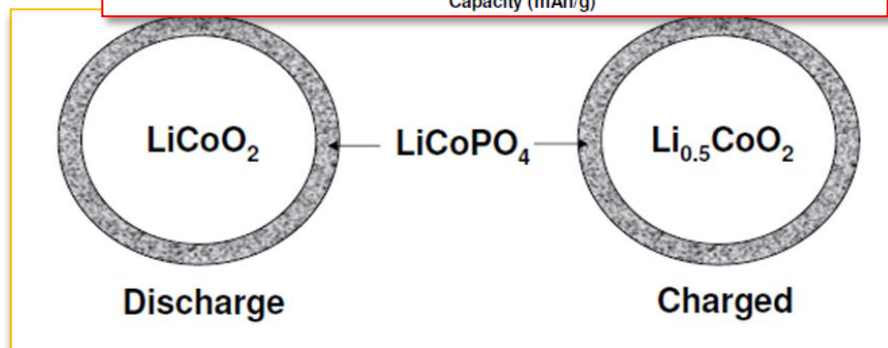
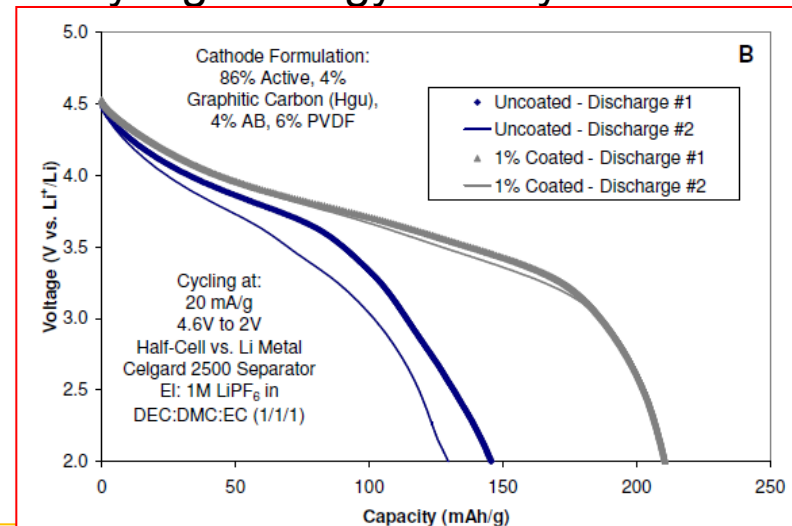
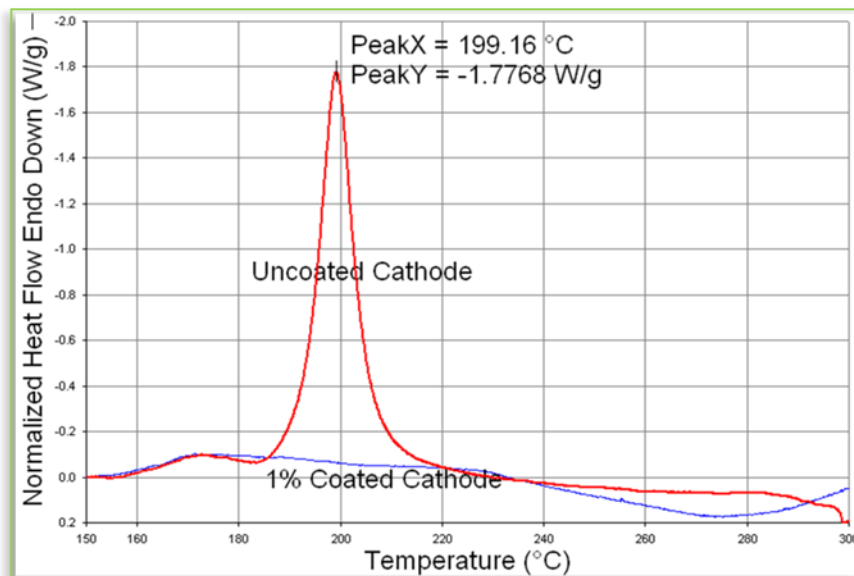
PSI

PSI formed lithium metal phosphate coatings on metal oxide cathodes by thermal treatment of a mixture of metal phosphate and the cathode.¹

¹ H. Lee, M. Kim, J. Cho, *Electrochemistry Communications*, 9 (2007) 149–154.

Benefits of Coating:

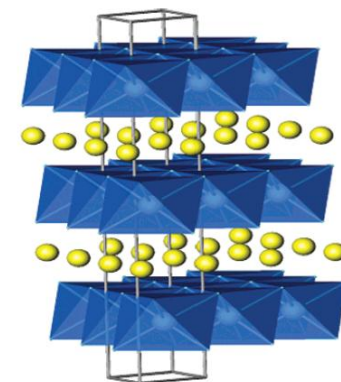
- Coating is a lithium conductor.
- Metal phosphates offer greater stability than their metal oxide counterparts.
- Coating technique can be applied to protect any high energy density cathode material.
- Common processing steps allow for low cost manufacturing.



Summary of Current Technology Work

- **High Energy NMC Cathodes**

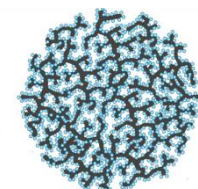
- Scale up of the NASA-process
- High Irreversible capacity loss, especially with uncoated cathode
 - Non-availability of lithium at the anode for the irreversible capacity.
- Electrolyte consumption (and anode dry out) due to O_2 evolved in formation
- Transition metal dissolution in electrolytes (Mn, Ni and Co)
- Low power densities, more noticeable with high electrode loadings
- Voltage slump during cycling due to “spinel formation”



HE-NMC Cathode

- **Si composite anodes**

- Limited cycle life (< 500)
- High irreversible capacity (10-20%) and poor coulombic efficiency
- Unknown compatibility with the high energy cathode (dissolved metal?)



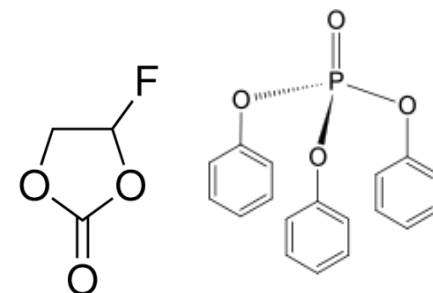
Nano-Si anode

- **Electrolytes**

- Changes to the cathode or anode may require electrolyte modification

- **Cell Design**

Test for performance and safety



FEC

Triphenyl phosphate
(TPP)

Li-O₂ and Li-air: ~ TRL 2

Characteristics:

Ultra-low mass

600 to 2200 mAh/g of cathode
depending upon current density (rate)

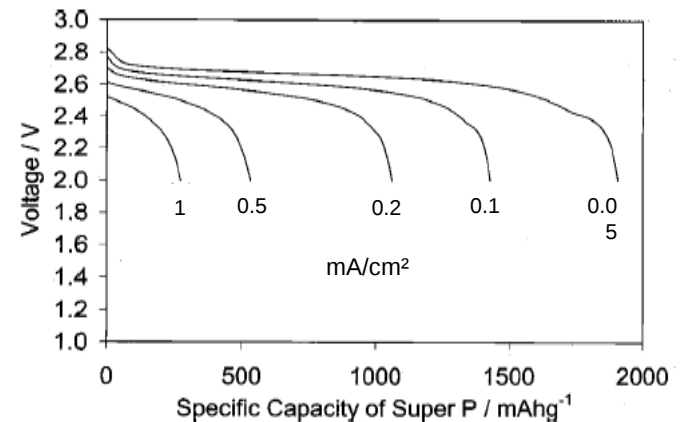
2.5 V avg. with 630 mAh/g carbon, 0.5
mA/cm²

Li-O ₂ and Li-air	Wh/kg	Wh/liter
electrochemical	587	880
pouch cell	473	617

2.3 V avg. with 300 mAh/g carbon, 1.0 mA/cm²

Li-O ₂ and Li-air	Wh/kg	Wh/liter
electrochemical	329	526
pouch cell	279	381

*Projections are for “free” air (neglect O₂ storage)



Journal of The Electrochemical Society, **149** (9) A1190-A1195 (2002)

Challenges:

- Recharge capability
- Capacity of carbon to store Li discharge products
- Rate capability

Oxygen storage type	Wh/kg	Wh/liter
steel	375	419
carbon composite	438	427
no storage	473	617

Li-S: ~ TRL 3

Characteristics:

High specific capacity (1600 mAh/g S theoretical)

2-plateau discharge

Projection for 2-plateau discharge
Assume 1000 mAh/g S

Li-S	Wh/kg	Wh/liter
electrochemical	610	864
pouch cell	474	595

Demonstrated in 4 Ah pouch cells (JSC):

BOL: 393 Wh/kg

EOL: 256 Wh/kg

75 cycles to 80% of initial capacity

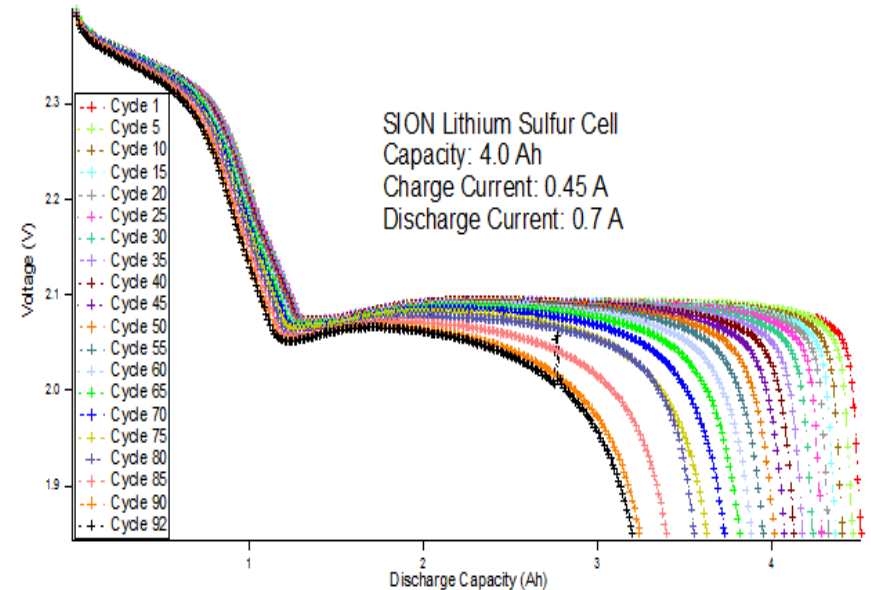


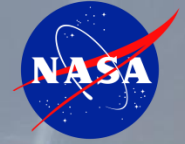
Figure 17: Sion Lithium Sulfur Cell ID# 20F Rate Capability Protocol #2 Data

Challenges:

Safety (rechargeability, lithium dendrite formation)

Cycle life

Challenges



- High Energy Density – equating to lighter mass and in many cases volume
- Very safe in a human-rated environment (includes ground handling and installation at launch facilities) – no fire, no thermal runaway
- Various pressure environments (pressurized, vacuum)
- Launch and landing loads (vibration, impact), etc.
- Sea water immersion (landing environment)
- Extreme temperatures
- Long-term missions with less maintenance

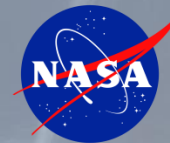


Acknowledgment

- Karunya University for inviting me to speak
- My Battery Group colleagues at NASA-Johnson Space Center, NASA-Glenn Research Center and NASA-JPL
- NASA Programs that fund the battery work

Back-up Slides

Failure Modes & Controls or Mitigation Measures for Li-Ion Batteries



Overcharge

Min. 3 controls
Verified by test
*Manuf. spec

Repeated Overdischarge/ Overdischarge followed by charge

Min. 3 controls verified
by test
*Manuf. Spec.

High temperatures/High Thermal Environments

*Thermal analysis leading to
appropriate thermal sensing;
3 Controls; Verified by test
Design qualified to extreme
temps *Manuf. Spec.

External Shorts High and Low Impedance

Controls and Design
for Minimum Risk
Verified by test;
*heat dissipation

Internal Short

Design for Minimum Risk
Stringent testing and
screening of flight cells;
manuf. facility audits
•Impeccable cell quality,
cell uniformity; Usage
within manufac.spec.
(latent defects, field
failures)

Stringent Monitoring and Control of

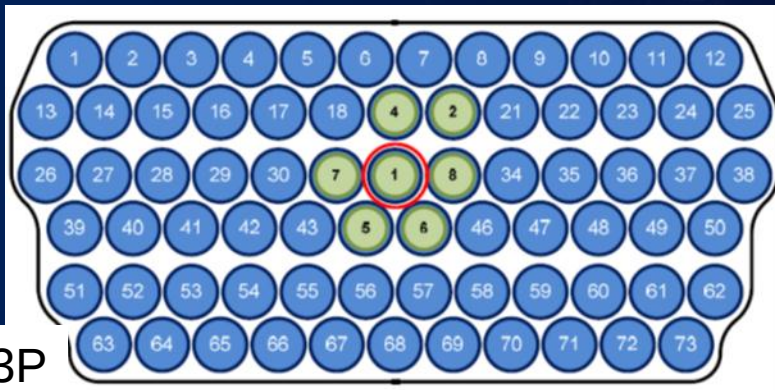
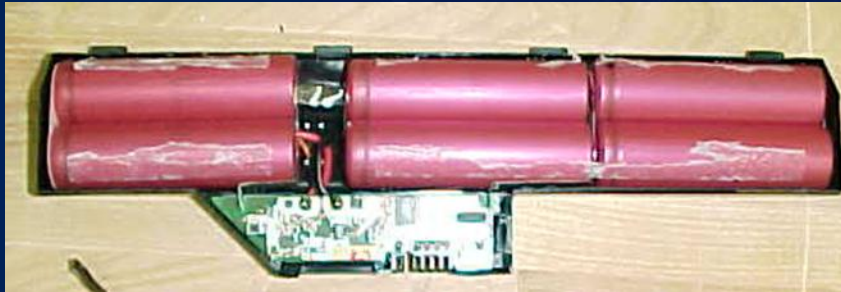
*Cell and battery voltage
*Battery current
*Temperature

Cell Balancing designed into a majority
of applications



Li-ion Battery Designs and Challenges

Thermal Gradient and Safety are major Challenges



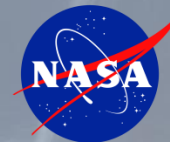
73P

Battery has 8 such banks in series
(Total of 584 cells 73P8S in one battery)



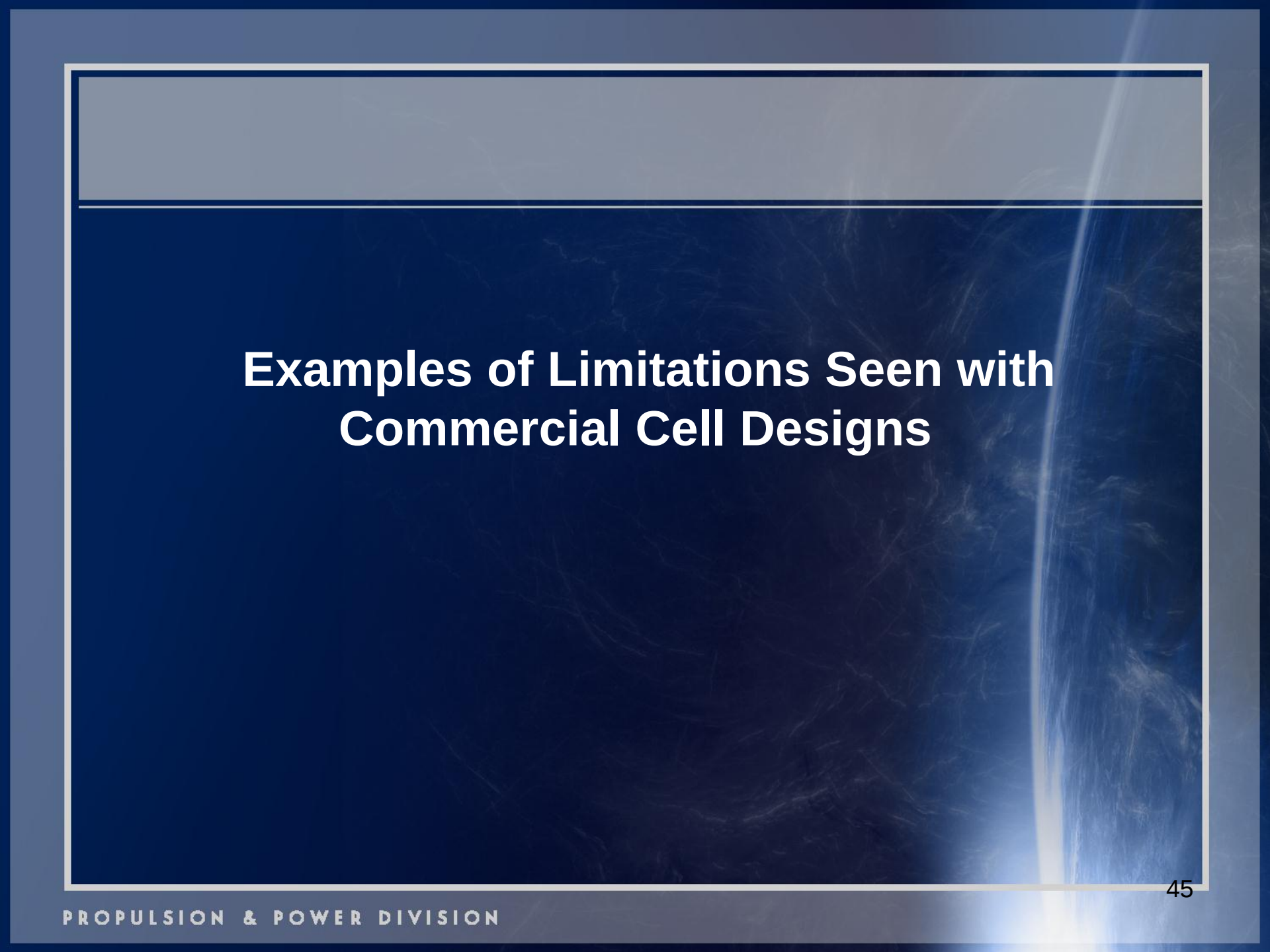
High Voltage/High Capacity

Concerns with Scaling & Testing: Cell to Module to Battery Level



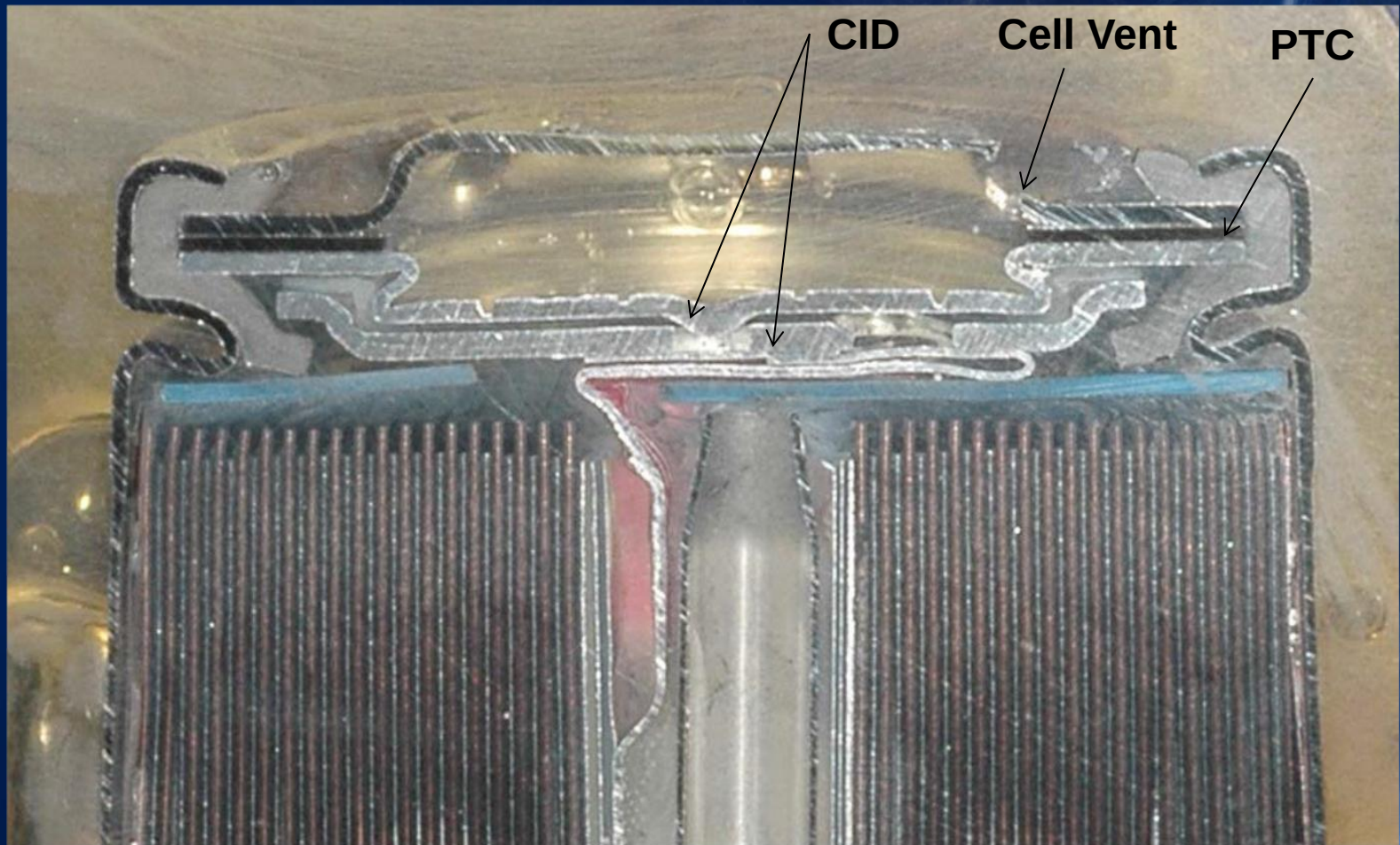
- Li-ion battery designs should have high fidelity thermal analysis to show that the battery design is safe under worst case environments (temperatures and pressures) and under all nominal and off-nominal conditions.
 - Results of thermal analysis should provide guidance on safe designs with very good heat dissipation paths.
 - Good thermal design increases safety as well as extends the life of the battery
- Li-ion battery management electronics should be robust
 - strike a balance in monitoring and control;
 - extensive testing of control electronics should be carried out on ground
 - For human-rated safety critical applications **insight into telemetry** should be appropriate for trouble-shooting off-nominal events.

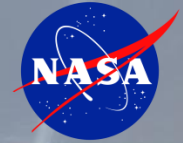




Examples of Limitations Seen with Commercial Cell Designs

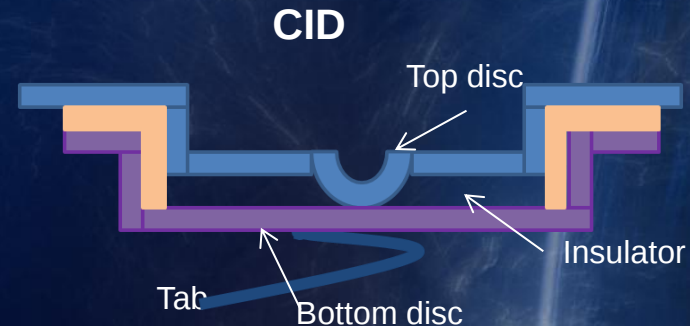
Li-ion 18650 Cell Cross-Section



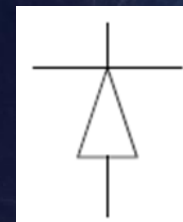


Examples of Cell Protective Devices

- Lithium-ion cells, whether cylindrical, prismatic, etc. irrespective of size, have different forms of internal protective devices
 - PTC
 - CID
 - Tab/lead meltdown (fusible link type)
 - Bimetallic disconnects
 - etc.
- External protective devices used in lithium-ion battery designs are
 - Diodes
 - PTC/polyswitch/contactors
 - Thermal fuses (hard blow or resettable)
 - Circuit boards with specialized wire traces
 - etc.



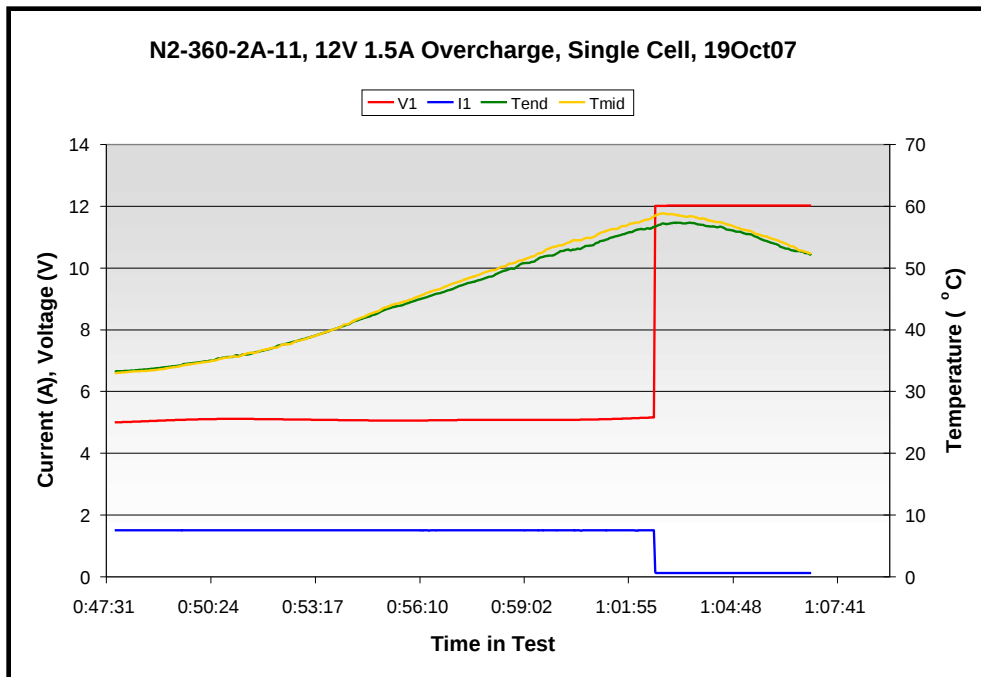
Diode



Although cell level protective devices protect cells and low voltage /low capacity batteries (less than 12 V and 60 Wh), extensive testing at NASA-JSC has shown that cell level protective devices do not always protect when the cells are used in batteries of high voltage and high capacity.



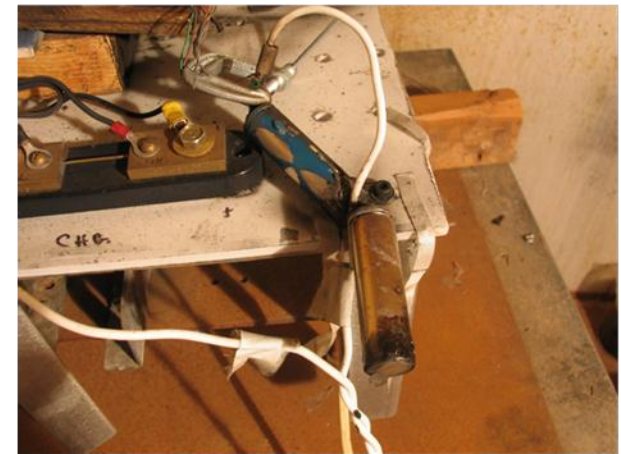
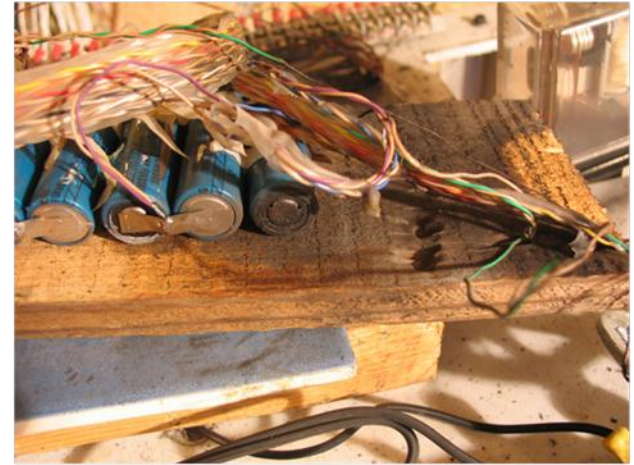
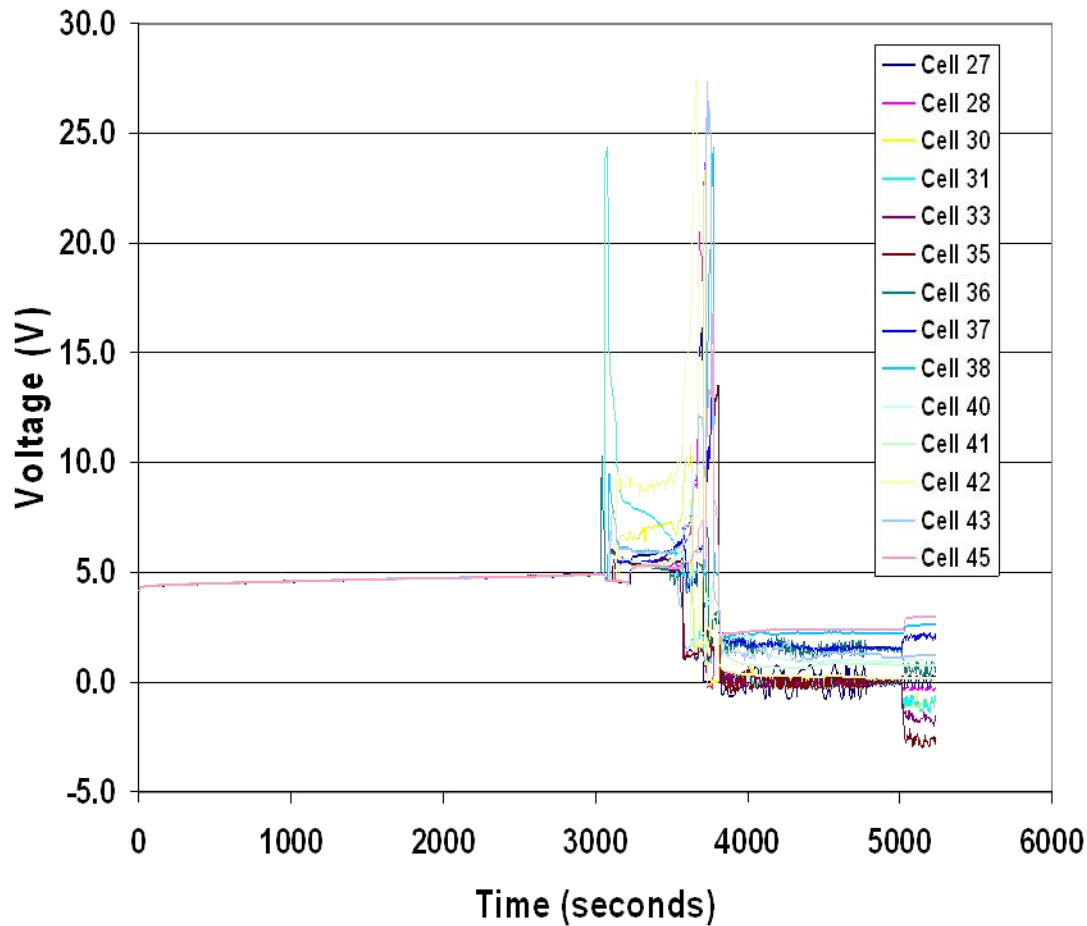
12V 1.5A Overcharge on Single Cells



•CID devices activated in both samples at 1 hour and 2 minutes into the overcharge.

	CID Open Time (approximate)	Sample Temp. at CID Open (°C)
N2-360-2A-11	1:02:38	59
N2-360-2A-12	1:02:28	73

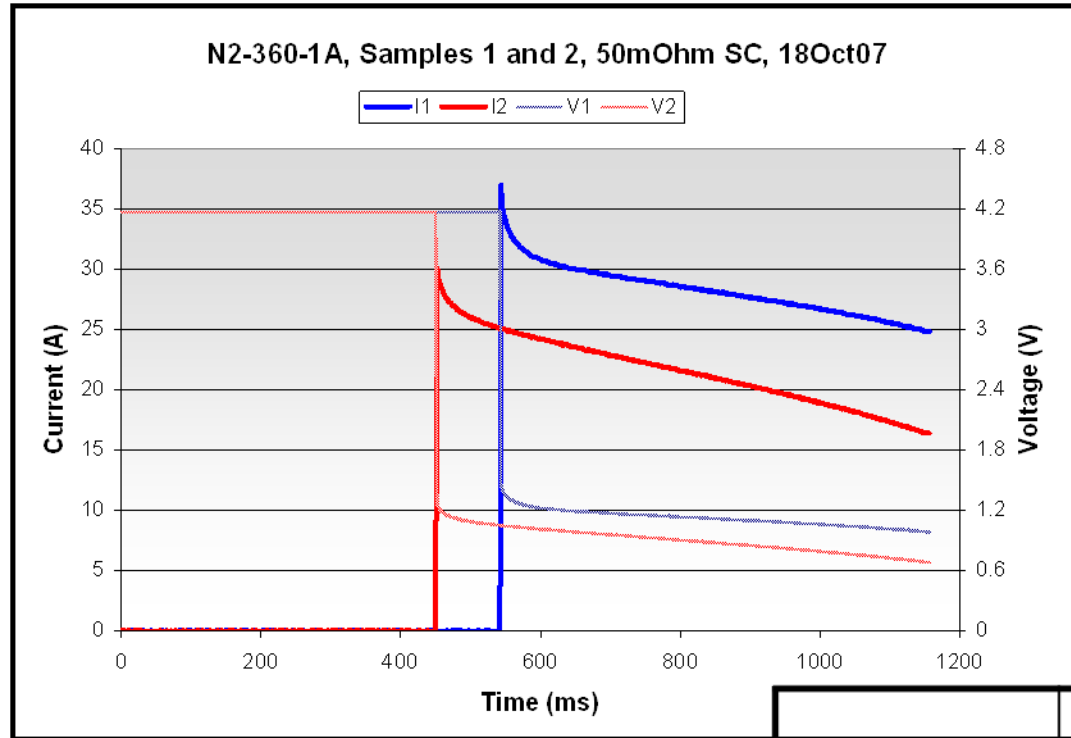
Overcharge Test on a 14-Cell String Showing Cell Voltages for the Sony Li-ion Cells



Missing : 27, 28, 30 and 31

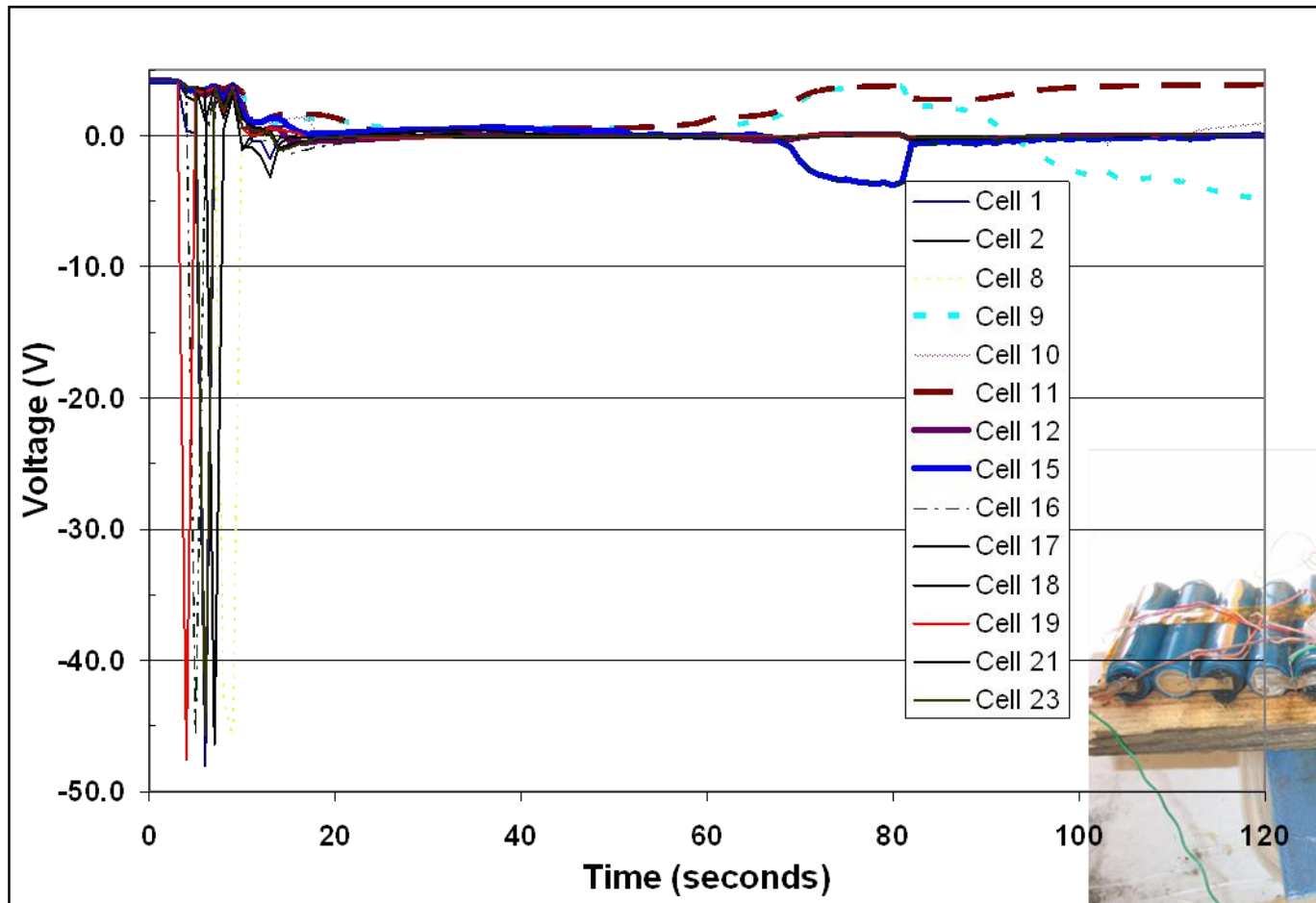
Cells 37, 38 and 45 showed no visible
Signs of venting

50mOhm Short Circuit, Single Cell (1000 Hz Chart)

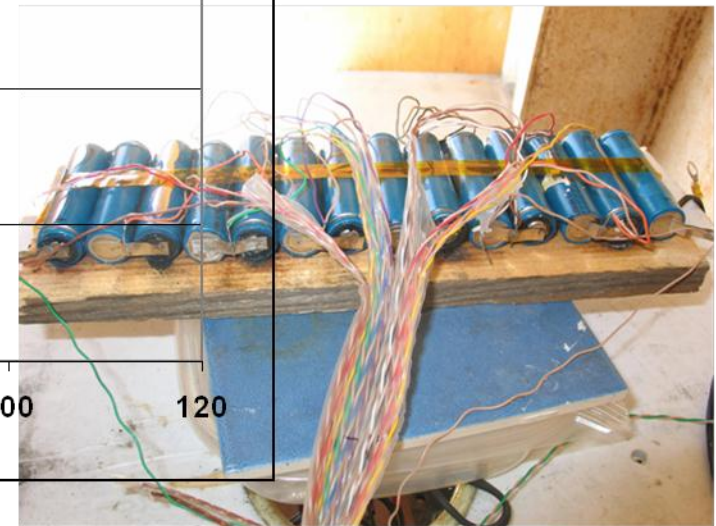


	Peak Current (A)	Peak Temp (°C)	Peak Temp Time (minutes)
N2-360-1A-1	37	78	43
N2-360-1A-2	30	82	49

14-Cell String Short Circuit Test on Sony Li-ion Cells

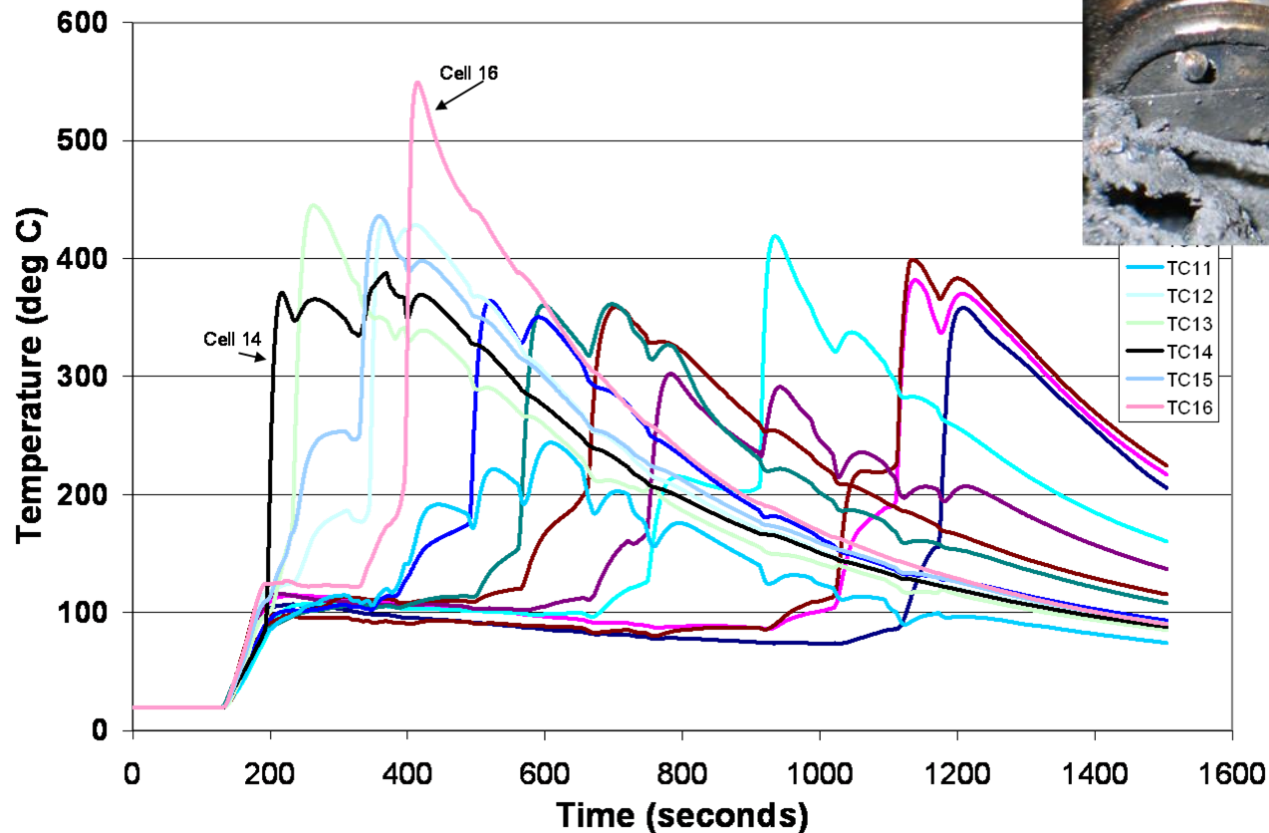


Only venting observed,
no fire
Cell Voltages in bold –
No visible signs of
Venting or damage,
but no voltage;
All others vented with
Obvious leakage or
discoloration

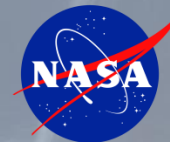


Rapid cell venting within the first 10 seconds

External Short Test on 14S Under Vacuum Conditions



Examples Showing Cell Limitations in Multicell Configuration



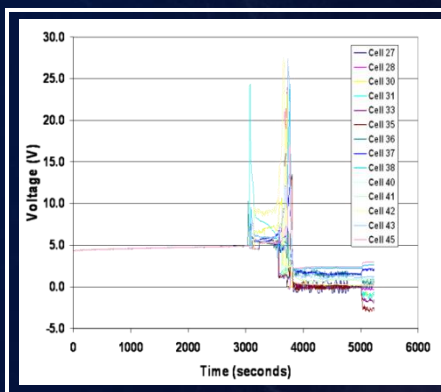
48V 6A Overcharge on 4P Battery



12V 6A Overcharge on 4P Battery



Photos show the limitations of 18650 size cells; These cells are only test vehicles; protective devices, internal and external to the cells, irrespective of cell size, should be fully characterized at all appropriate levels if used within the first three levels of safety control.



Overcharge Test on a 14-Cell String



External Short on 8S5P Matrix Pack



Summary of COTS li-ion cell limitations

- Test in the relevant configuration, environment, understand and characterize limitations

Test, design, retest, redesign,.....pattern required for confirmation of safety

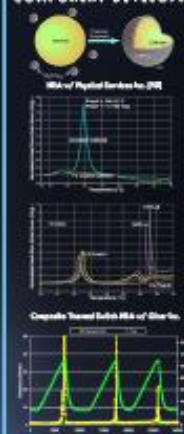


BATTERY SYSTEMS

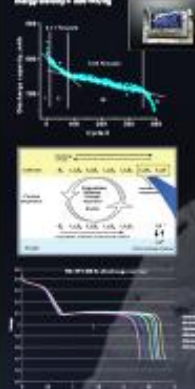
GOVT. FURNISHED EQUIPMENT



ETOP/ETDO SAFETY COMPONENT DEVELOPMENT

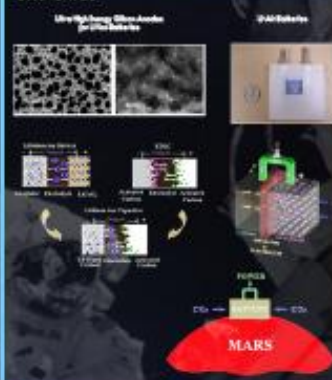


LI-S WITH SION POWER



RESEARCH & DEVELOPMENT

BASIC R&D



COLLABORATIONS



OTHER ENGINEERING / SAFETY SUPPORT

